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Flocculation and Clarification of Mineral Suspensions

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16. Abstract

Starch and calcium chloride were used as flocculants in a study of the flocculation and clarification characteristics of quartz and geothite suspensions. Settling rates of the suspensions, the amount of suspended solids in the supernatant liquid and the concentrations of the residual starch and calcium ion were monitored. The effects of the size distribution and the pulp dilution of the minerals, of the temperature, and of the chemical modification of the starch structure were also investigated. Goethite suspensions were shown to be readily flocculated with clear supernatant liquid using starch over a wide range of pH, whereas quartz suspensions could not be flocculated with starch in the absence of calcium ion. The resultant supernatant liquid was extremely difficult to clarify, even in the presence of an excessive amount of calcium ion. A cationic starch of a certain molecular size and degree of substitution or a combination of a polymeric compound and a cation capable of reversing the charge of the quartz showed some promise in the clarification of quartz suspensions. The most effective flocculation and clarification condition was observed when a polymeric compound was adsorbed uniformly in sufficient quantity and in a stretched-out conformation, and when the zeta potential of the resulting suspension was made close to zero. (Lowry-Texas)

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ABSTRACT

A study of the flocculation and clarification of quartz and goethite suspensions using starch and calcium chloride as flocculants was made by determining the settling rates of the suspensions, the amount of suspended solids in the supernatant liquid, and the concentrations of the residual starch and calcium ion. These determinations, supplemented with measurements of streaming potential, adsorption density, and viscosity, were used to formulate a comprehensive expression of the mechanism involved in the use of starch flocculants. No particular difficulties were experienced either in the flocculation or in the clarification of goethite suspensions. Quartz suspensions, particularly when aged in alkaline solutions, were extremely difficult to clarify. A cationic starch of a certain molecular size and degree of substitution or a combination of a polymeric compound and a cation capable of reversing the charge of the quartz showed some promise in the clarification of quartz suspensions. The maximum settling rates and the minimum turbidity of the supernatant liquid for a given condition were observed at a point where an excess of starch began to appear in the solution. The most effective flocculation and clarification condition may be observed when a polymeric compound is adsorbed uniformly in sufficient quantity and in a stretched-out conformation, and when the zeta potential of the resulting suspension is made as close to zero as possible. This report was submitted in fulfillment of Grant No. 14010 DRB from the Federal Water Quality Administration to the University of Minnesota.

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SECTION I

SUMMARY AND CONCLUSIONS

Flocculation and clarification behaviors of quartz and goethite suspensions having identical size distribution were studied by determining the settling rates, the amounts of suspended solids in supernatant liquid, and the residual calcium and starch concentrations using a combination of calcium chloride and corn starch. The effects of the size distribution and the pulp dilution of the minerals, of the temperature, and of the chemical modification of the starch structure were also investigated. Streaming-potential measurements, correlated with the adsorption data of starches on minerals and with the viscosity measurements on starch solutions, clarified the role each additive plays in flocculation. The information thus gathered was utilized also to the selective flocculation of a mixture of quartz and goethite.

The following mechanism of flocculation using starches has been deduced from the experimental results and from the previous knowledge appearing in literature and used in the discussion of the results. Flocculation of a mineral suspension with a starch is effected by bridging of particles by the adsorbed starch molecules. The adsorption density and the conformation of the adsorbed starch governs the flocculation behavior. The adsorption of starch molecules on oxide minerals results from hydrogen bonding, but is strongly influenced by the electrostatic interaction between the charged functional groups in a starch molecule and the charged mineral surface. The electrical double-layer theory in conjunction with the adsorption measurements and the streaming-potential measurements provides a useful guide in interpreting the adsorption behavior. The conformation of a starch molecule may be altered through an introduction of charged functional groups in the starch structure, or through an addition of an electrolyte to the solution. A stretched-out conformation facilitates the bridging, but an excessive introduction of the charged functional groups interferes with bridging through intermolecular repulsion. A high concentration of an electrolyte makes the starch molecules coil up and the bridging less effective. Viscosity measurements provide a convenient technique for investigating the conformation of starch molecules. The clarification of the fine turbidity by the suspended solids may be effected when the zeta potential is reduced to near zero. A polymeric flocculant of too high molecular weight often results in an excess local concentration which produces irreversible stabilization by protective action. In this respect corn starch appears to be more ideally suited in studying the flocculation and clarification behaviors of mineral suspensions than high molecular-weight synthetic polymers.

The results of the present investigation lead to the following conclusions:

1. Goethite suspensions could be readily flocculated with clear supernatant liquid using starch over a wide range of pH.

2. Quartz suspensions could not be flocculated with starch in the absence of calcium ion. The supernatant liquid was extremely difficult to clarify even when an excessive amount of calcium ion was added along with a starch or a polyelectrolyte.

3. The condition for maximum settling rate and minimum turbidity after settling was observed at a starch level where an excess of starch begins to appear in the supernatant liquid. The critical amount of starch for this condition was dependent on the type and the mesh-of-grind of mineral, the type of starch, the pulp pH and the calcium ion concentration.

4. Adsorption of starch molecules on an oxide mineral depends on the molecular size and the substituted charged functional group in the starch structure, the pulp pH and the calcium ion concentratration. Goethite adsorbed appreciably more starch than quartz for a given condition.

5. The isoelectric points of quartz and goethite were determined by streaming-potential measurements to be at pH near 2 and 6.7 respectively. Negatively-charged quartz and goethite surfaces may be made positive in calcium chloride solutions only in highly alkaline solutions. This observation supports a view that a hydrolyzed species $CaOH^+$ is responsible for the reversal of charge.

6. Streaming-potential measurements indicated that the adsorption of corn starch on goethite was irreversible, and the adsorption on quartz in the acid pH range appeared to be also irreversible.

7. Cationic starch was particularly effective in clarifying quartz suspensions. An excessive substitution of the starch structure with cationic groups, however, appeared to interfere with flocculation due to interparticle repulsion.

8. Anionic starch (0.93 D.S.) was ineffective in clarifying quartz suspensions irrespective of pH and of calcium chloride concentration. It was also ineffective in flocculating goethite suspensions of highly alkaline pH.

9. The floc size appeared to be determined by the amount and the conformation of starch adsorbed, thereby controlling the settling as well as the filtration rates.

10. The clarities of supernatant liquids were, in general, not related to the settling rate, and appeared to be governed by the zeta potential. Too strong an affinity of poly-

meric flocculant due to high molecular weight or to a favorable chemical modification resulted in high turbidity in the supernatant liquids. Locally excessive concentration of the polymeric flocculant caused irreversible stabilization, particularly of fine particles, by protective action.

11. Viscosity of a corn starch dispersion decreased as the concentration of calcium ion in solution increased. This electroviscous effect was more pronounced at higher pH.

12. The maximum settling rate of a goethite suspension flocculated with corn starch at natural, near neutral pH and at pH 11 decreased with increasing concentration of calcium ion due to coiling of the adsorbed starch molecules.

13. The maximum settling rate of a quartz suspension flocculated with corn starch at natural, near neutral pH decreased, whereas the rate at pH 11 increased markedly with increasing concentration of calcium chloride. This increase in the rate up to 10^{-1}N calcium chloride was due to increased adsorption of the starch, but the rate eventually decreased at a high concentration of calcium ion due to coiling of the adsorbed starch molecules.

14. The maximum settling rate of a flocculated suspension for a given condition increased somewhat as the size distribution of that mineral became coarser. Pulp dilution had a pronounced effect on the maximum settling rate; whether the maximum settling rate increased or decreased with the pulp dilution appeared to depend on the affinity of starch towards the mineral surface. In either case, dilute suspensions were shown to be difficult to clarify.

15. Both the settling rate and the supernatant liquid improved with increasing temperature. The effect of temperature, however, was less than that expected from the decrease in viscosity alone.

16. Selective flocculation of a mixture of goethite and quartz could be effected using corn starch as a flocculant. The pulp pH and the level of starch addition were identified to be some of the important variables.

SECTION II

RECOMMENDATIONS

Of immediate interest in applying the findings of the present investigation is the clarification of the siliceous tailings from magnetite-taconite plants and of the dispersed siliceous slimes as well as the water reuse in the selective desliming-flotation process on nonmagnetic taconites. As reported in this article, quartz suspensions, particularly those aged in alkaline solutions, are extremely difficult to clarify.

It is recommended that test programs on the treatment of magnetite-taconite tailings and of dispersed siliceous slimes from selective desliming operations be considered in a small-scale pilot plant in order to develop a sensing device for monitoring the clarification behavior in a continuous stream. Based on the results of the present investigation, measurements of the residual concentrations of starch and calcium ions, and of the pulp pH may be related to the clarity of the supernatant liquid from a thickener, leading eventually to an automatic control system. In this manner the clarification of the supernatant liquid will be maximized, yet the pollution due to excess starch and calcium ion in the effluent will be minimized.

Though a certain degree of success in clarifying quartz suspensions has been attained using cationic starch or a combined use of dodecylammonium ion and starch, a search for more effective means of clarifying quartz suspensions should be considered. Some of the flocculants suggested in this report are cationic starches of different molecular weights and degrees of substitution, and such modifying agents in conjunction with starch as magnesium, aluminum, ferric, and dodecylammonium ions.

In addition, an extension of the present approach to calcite, another major constituent mineral in many iron ores and nonferrous metal ores, becomes of both theoretical and practical interest. Calcite is a salt-type mineral and the characteristics of its adsorption of polymeric flocculants differ greatly from those of oxides. Furthermore, calcite releases calcium ions into pulp liquors. The presence of calcite in magnetite-taconite tailings may influence their flocculation behavior and may also determine the effectiveness of separation in the selective desliming of nonmagnetic taconites.

SECTION III

INTRODUCTION

The clarification of plant effluents, particularly those from mineral processing operations, is becoming of much concern for the prevention of stream and lake pollution. For example, magnetite-taconite concentrators, base metal operations, such as copper, lead, and zinc, and uranium leaching plants, produce siliceous tailings. Coal washeries reject argillaceous tailings, and oxidized iron ore plants discharge red iron ore slimes. The effects of such flocculants as multivalent cations[1] and polymeric compounds[2,3] have been the subject of much investigation. The former is explained by the lowering of the electrokinetic potential and the latter usually by polymer bridging. The effectiveness of the combined use of a multivalent cation and a polymeric compound has often been quoted in literature,[4,5,6,7] but little information is available on their individual roles and their interaction with respect to sedimentation rate and clarification of the supernatant water. The beneficial effect of the presence of coarse particles in suspension has been recognized,[8] but the relation between the size distribution characteristics and the flocculation behavior has not been well established.

In a recent study at the Mineral Resources Research Center* on the use of calcium chloride and starches in iron ore beneficiation,[9] it was noted that the sedimentation rates and the filtration rates of red iron ore slimes and of magnetite-taconite tailings were strongly dependent on the starch concentration, whereas the clarity of the supernatant water depended on the calcium-ion concentration and the pH, and the extent of their interaction was determined by the mineralogy of the suspension. It was speculated that the adsorbed starch through polymer bridging governed the floc size and the calcium-ion concentration and the pH controlled the zeta potential of the mineral, thereby controlling the clarity of the supernatant solution. Another notable observation was that an excess starch tended to redisperse the particles due presumably to its protective action. Not only for efficient utilization of these flocculating agents on the settling and clarification of mineral suspensions, but also for minimizing the pollution of effluents by these reagents it is desirable to formulate the nature and extent of their adsorption and to correlate with their flocculation and clarification behavior using certain pure mineral suspensions and their mixtures.

The present study was undertaken in order to examine the mechanism of a combined use of a multivalent cation and a polymeric compound, to arrive at a most effective choice in their use as flocculants for the control of water pollution problems, and to establish the effect of size only from p. 1

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*Formerly known as the Mines Experiment Station.

distribution on floc formation and clarification. For prototype solids, quartz and goethite of several different size distributions were chosen, since their grinding characteristics[10] and their surface properties[11,12,13] are fairly well established. At the same time they constitute the main components of the ore minerals of immediate interest for the iron ore industry of Minnesota. For flocculants, calcium ion and unmodified corn starch were used mainly because their analytical procedures are well established[14] and a certain amount of adsorption[6,15] and flocculation data, particularly on ores and tailings,[7] are available. The investigation was later extended to include chemically modified starches and polyelectrolytes.

SECTION IV

EXPERIMENTAL MATERIALS

Quartz and goethite samples used in the tests were prepared in the following manner.

Quartz

For flocculation and filtration tests a quartz sample was prepared from St. Peter sand by first agitating a 1000-gram sample in a Fagergren laboratory flotation machine using distilled water for 10 minutes, stopping the agitation to allow all plus 20-micron particles to settle, and then removing the supernatant slimes by siphoning. The cycle of brief agitation, sedimentation, and siphoning was repeated six times. The deslimed products thus prepared were heated overnight in a hot solution of 1 N hydrochloric acid and then repeatedly washed with distilled water until there was no response to the silver nitrate test for chloride ion. Approximately 40 pounds of the quartz sample was prepared in this manner and dried at 110° C.

The quartz samples for flocculation and filtration tests were prepared by dry-grinding 600-gram lots of the cleaned St. Peter sand in an Abbé porcelain mill for 30, 60, 120, and 240 minutes. The size distributions of the ground products, as determined by the Andreasen pipette method, are shown in Figure 1 (a). As apparent in the figure, the experimental data points are represented with straight lines having the same slope, but are shifted laterally as the grinding time is increased. Each line could be represented by the Schuhmann equation

$$y = 100 \left(\frac{x}{k}\right)^m$$

where y is the cumulative percent weight finer than size x, and m and k are respectively the distribution and size moduli. The distribution modulus, or the slope, is seen to remain constant at 0.79 and the size moduli at 330, 138, 60, and 26 microns, respectively. Figure 2, in which the size moduli are plotted against the grinding time, shows another straight line relationship.[10] The Blaine surface areas of the last three samples were 1320, 2860, and 5110 cm^2 per gram.

For streaming-potential measurements three types of quartz samples, viz., St. Peter sand, Montana pegmatite quartz, and Brazilian rock crystal, were compared in a series of preliminary tests, and eventually Brazilian quartz was selected for a detailed study of the effect of starch, calcium chloride, and pH. All the samples used in the streaming-potential measurements were prepared by screening out a 48/65-mesh fraction, treating it in hydrochloric acid solutions of different strengths for a specified length of time, and then washing it with distilled water until there

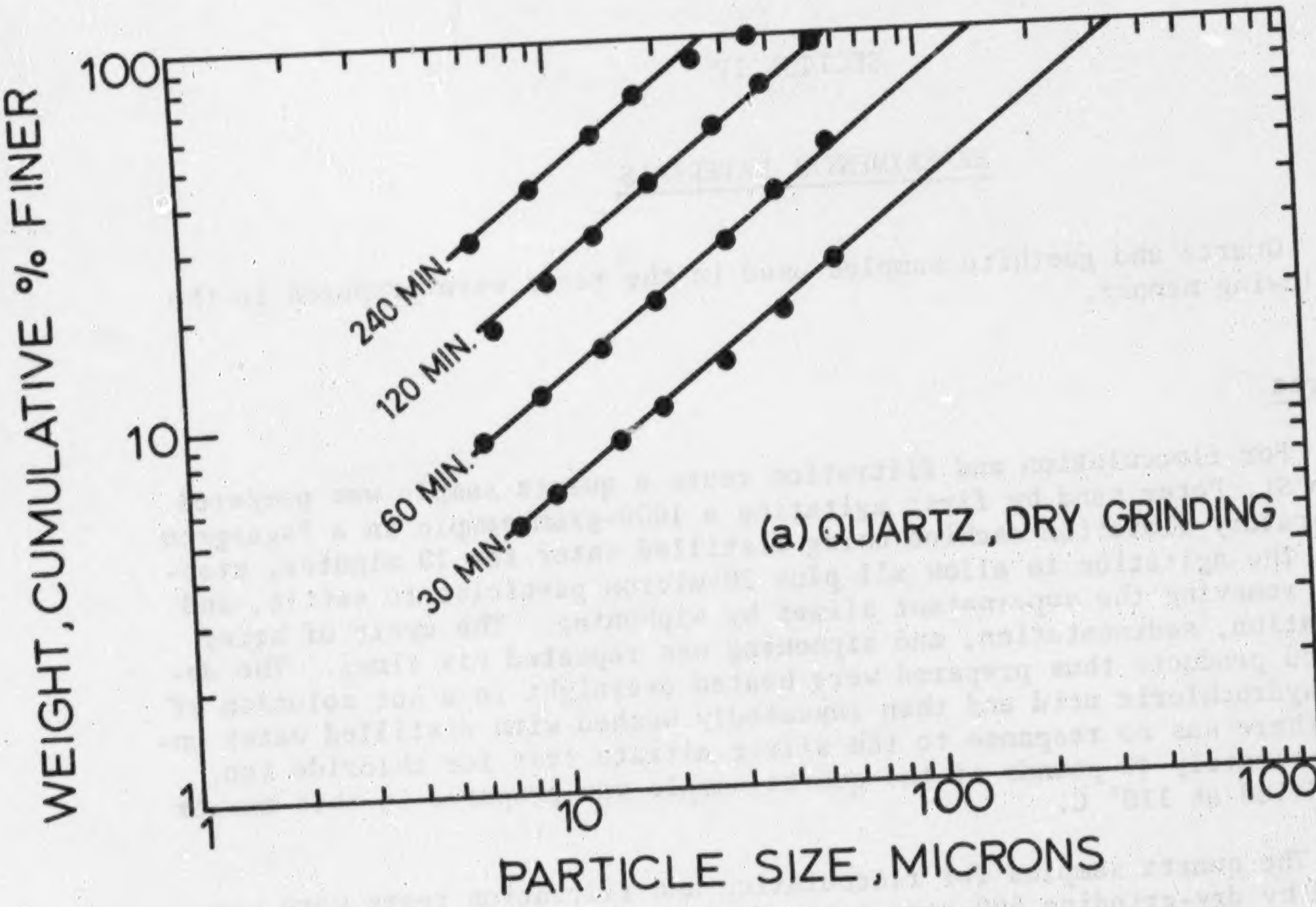

FIGURE 1(a). Size Distribution of Quartz as a Function of Grinding Time

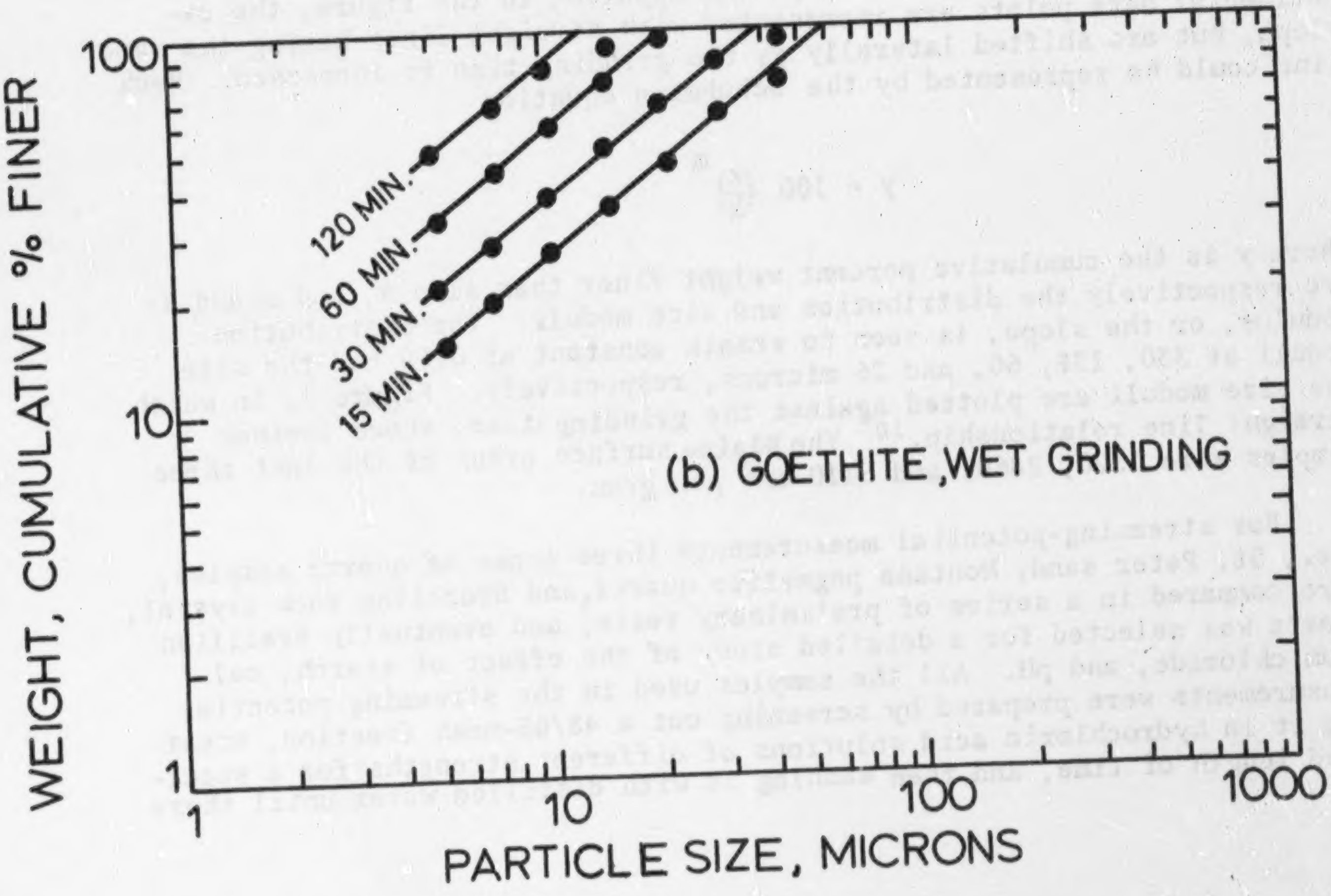

FIGURE 1(b). Size Distribution of Goethite as a Function of Grinding Time

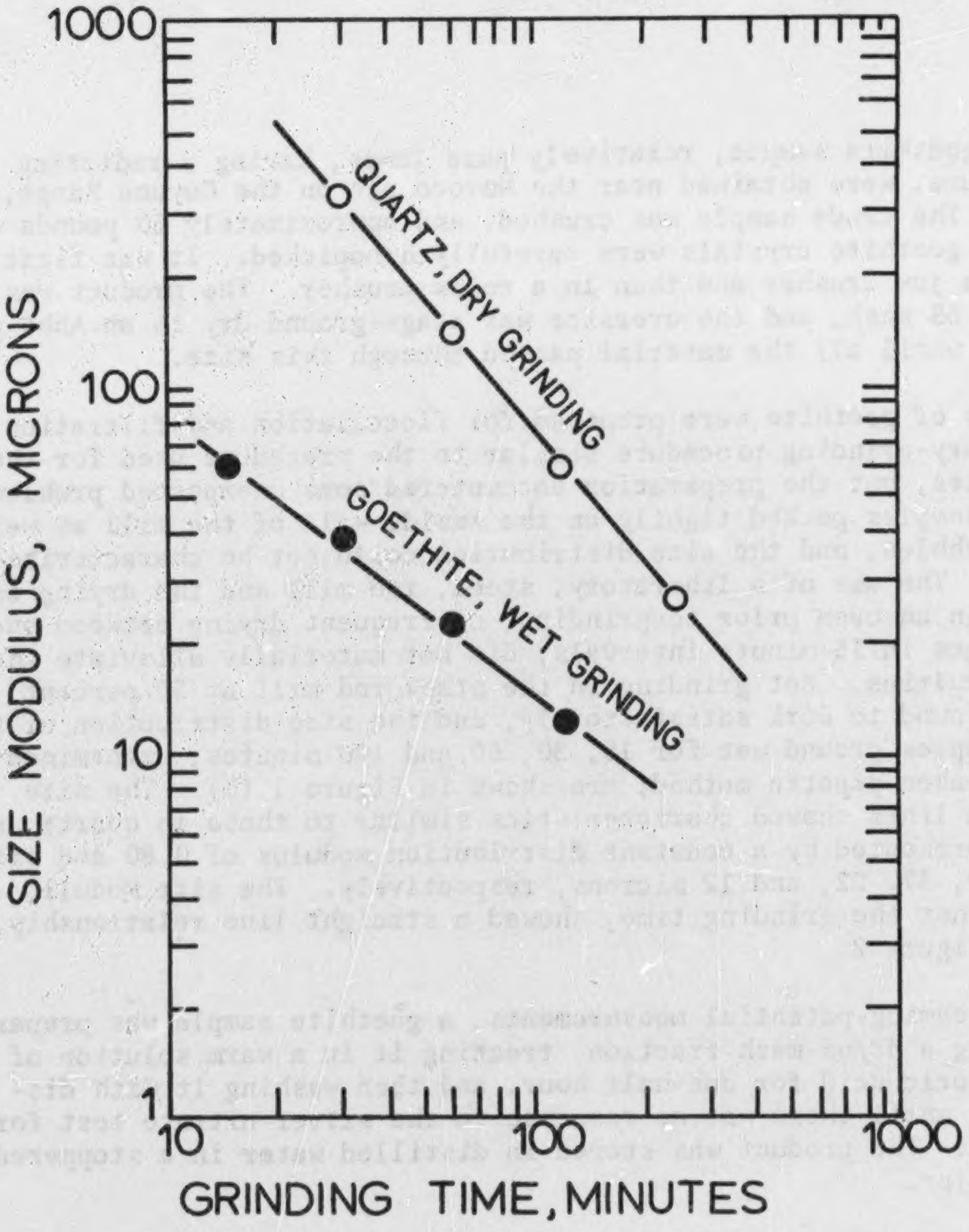

FIGURE 2. Grinding Time - Size Modulus Relationships for Quartz and Goethite

was no response to the silver nitrate test for chloride ion. The details of the cleaning procedure for the three types of quartz samples and the results of the preliminary tests are given in Experimental Results section. All the samples were stored either in distilled or in demineralized water in a stoppered Pyrex glass jar.

Goethite

For a goethite sample, relatively pure lumps, having a radiating fibrous structure, were obtained near the Marcco pit on the Cuyuna Range, Minnesota. The crude sample was crushed, and approximately 50 pounds of high-purity goethite crystals were carefully handpicked. It was first crushed in a jaw crusher and then in a rolls crusher. The product was screened at 65 mesh, and the oversize was stage-ground dry in an Abbé porcelain mill until all the material passed through this size.

Samples of goethite were prepared for flocculation and filtration tests by a dry-grinding procedure similar to the procedure used for the quartz samples, but the preparation encountered some unexpected problems. The ground samples packed tightly on the inside wall of the mill as well as on the pebbles, and the size distribution could not be characterized as readily. The use of a laboratory, steel, rod mill and the drying of the sample in an oven prior to grinding, or frequent drying between successive stages in 15-minute intervals, did not materially alleviate the above difficulties. Wet grinding in the steel rod mill at 50-percent solids was found to work satisfactorily, and the size distribution of the goethite samples ground wet for 15, 30, 60, and 120 minutes, determined by the Andreasen pipette method, are shown in Figure 1 (b). The size distribution lines showed characteristics similar to those in quartz, and could be represented by a constant distribution modulus of 0.80 and size moduli of 60, 37, 22, and 12 microns, respectively. The size moduli, plotted against the grinding time, showed a straight line relationship, as seen in Figure 2.

For streaming-potential measurements, a goethite sample was prepared by separating a 48/65-mesh fraction, treating it in a warm solution of 1 N hydrochloric acid for one-half hour, and then washing it with distilled water until there was no response to the silver nitrate test for chloride ion. The product was stored in distilled water in a stoppered Pyrex glass jar.

For most of the tests on flocculation and filtration, quartz and goethite samples that had approximately the same size modulus were chosen, namely, the quartz sample dry-ground for 120 minutes and the goethite sample wet-ground for 15 minutes. Both samples had a size modulus of 60 microns and a distribution modulus, coincidentally, of approximately 0.8. The ground sample of goethite was filtered and split into 50-gram (dry basis) lots. Each lot was kept moist in a sealed container until it was used. The chemical composition of the goethite sample thus prepared was as follows:

Fe	57.10%
Mn	1.39
SiO_2	3.11
H_2O (400°C)	8.02
(800°C)	10.53
Al_2O_3	0.75

Starches

The following four starches received from Corn Products Company, Argo, Illinois, were used for the present investigation.

Corn Starch (Globe Pearl No. 3001)
0.023 D.S. Cationic Starch
0.067 D.S. Cationic Starch
0.93 D.S. Carboxymethyl Corn Starch, Sodium Salt

Globe Pearl Starch 3001 is a corn starch which has been prepared with a minimum alteration. The cationic starches are laboratory samples prepared by derivatizing unmodified, pregelatinized corn starches to introduce aminoethyl groups into the starch structures. Anionically modified carboxymethyl starch is also a laboratory sample prepared in a similar manner as above.[16] The definition of the degree of substitution (D.S.) is given on page 90.

Synthetic Polymers

The four synthetic polymers used in the present investigation were received from Dow Chemical Company, Midland, Michigan, and were reported to have the following characteristics.[17]

	Ionic Character	Nominal Molecular Weight
Separan NP-10	Non-ionic	1×10^6
Separan NP-20	Non-ionic	2×10^6
Separan AP-30	Anionic	$>2 \times 10^6$
NC 1733	Cationic	1×10^6

Dodecylammonium Chloride

Dodecylammonium chloride was prepared[12] by bubbling dry hydrogen chloride gas through a 20-percent solution of high-purity dodecylamine, received from Armour and Company, in anhydrous benzene. The crystals of dodecylammonium chloride (DAC), precipitated on cooling to room temperature, were filtered, washed thoroughly with benzene, and transferred to a flask with a reflux water condenser. The material was heated over a water bath until all the solids had been dissolved. It was cooled, filtered, and washed with benzene, and the process of recrystallization was repeated twice. Finally, a 5-percent solution of methanol in benzene was used to produce large, well-defined crystals. The amine salt was filtered, dried, and evacuated in a vacuum desiccator to remove the adhering benzene and methanol.

Chemical Reagents

The reagents used in regulating the pH, such as sodium hydroxide and hydrochloric acid, anhydrous calcium chloride, potassium chloride, and aluminum nitrate, were of analytical reagent grade.

Water

Distilled water was used for flocculation and filtration tests. Demineralized water, containing less than 0.1 ppm of salts as NaCl, was used for streaming-potential measurements and unless stated otherwise in the preparation of all solutions and for all test work.

SECTION V

EXPERIMENTAL PROCEDURE

The procedures used for preparing starch and polyelectrolyte solutions, for testing the flocculation and filtration behaviors, and for measuring the zeta potentials and viscosities were as follows.

Preparation of Starch Solution

Since the pulp* pH was to range between 3 and 12 in the test program, and since the presence of excessive inorganic ions added for the adjustment of the pH was expected to influence the flocculation behavior as well as the zeta-potential measurements, it was thought necessary to avoid the use of caustic soda for the solubilization of corn starch. The starch solution was, therefore, prepared by heating in an autoclave at 125° for 30 minutes, followed by a rapid cooling in a water bath, and then homogenizing in a Waring blender for 30 seconds.

The starch solution thus prepared was examined under a microscope to confirm that all the starch granules had been ruptured to form a colloidal dispersion.[6] In addition, a few preliminary flocculation tests were made with this solution and the results were compared with a causticized starch solution. Virtually identical results justified the present preparation method for the following tests, unless stated otherwise. To minimize the effects of microbiological decomposition, fresh starch solutions were prepared each day. Chemically modified starches, both cationic and anionic, were solubilized in the same manner.

Preparation of Synthetic Polymer Solutions

The Separan samples were solubilized to 0.1-percent solutions by agitating them in a beaker on a magnetic stirrer. Two to four hours were required for complete solubilization; the higher molecular weight Separans took longer times. The cationic polymer NC 1733 tended to clump in water and, therefore, the concentration of the stock solution was reduced to 0.01-percent. Fresh synthetic polymer solutions were prepared each week.

Flocculation Test Procedure

The flocculation test procedure was standardized as follows. Fifty grams (dry basis) of a sample was placed in a 1000-ml graduated cylinder and diluted with make-up water to near the 1000-ml mark so that the subsequent addition of reagent would give a total pulp volume of 1000 ml. At this point the pH of the pulp was adjusted to a desired value using sodium hydroxide. A predetermined amount of calcium chloride was then added and mixed thoroughly by inverting the cylinder ten times. This was followed by the addition of starch solution in three equal portions, mixing being performed between each addition by gently inverting the cylinder three times between each addition. After the final addition of starch, the cylinder was inverted five times, set down, and the settling rate was determined.

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*The word 'pulp' refers to a mixture of a ground ore with water.

To investigate the effect of agitation on settling rates, the pulp from the initial settling test was re-agitated for a second and a third settling test by inverting the cylinder five times between the successive tests. Typical experimental results thus obtained are shown in Figure 3(a). The settling rates were obtained from the straight line portion.

For quartz suspensions, particularly when the amount of calcium chloride was low, a well-defined pulp line was not observed and the above procedure could not be applied. A 1000-ml graduated cylinder was completely covered with a black tape except for an opening for the incident light from a 40-watt bulb and for the photocell of Photovolt No. 200 Universal Photometer at 19.4 cm below the 1000-ml mark. The pulp was agitated in the identical manner as above and the photometer reading was recorded as a function of time. A typical result is shown in Figure 3(b), from which the time required for the pulp line to fall the said distance is estimated to be 2.5 minutes, and the settling rate 3.06 inches per minute. When no calcium chloride was added the curve thus obtained showed no discontinuity. It was interpreted, therefore, that the pulp did not flocculate. Under such a condition the settling of the particles was expected to be extremely slow, and the settling rate of zero was assigned arbitrarily.

After the settling test, approximately 300 ml of the supernatant water was siphoned out and some of the solution samples were centrifuged at a speed sufficient to remove suspended solids without appreciably sedimenting the starch. The concentration of starch in the solutions was determined colorimetrically[18] and the concentration of calcium ion also colorimetrically using the purpurate method.[19] The amounts of the suspended solids were determined by pipetting 50 ml from the well-agitated supernatant solution, evaporating to dryness, and weighing the residue. The weights were corrected for soluble salts by comparing the dry weights with equal volumes of the respective solutions centrifuged to remove the suspended solids.

Filtration Test Procedure

For the filtration tests a Baroid No. 300 filter press with a cross-sectional area of 0.05 square foot was used. Except that one hundred grams (dry basis) of the sample was pulped to a total volume of 400 ml, the conditioning procedure of adjusting the pH, of adding first the cal-

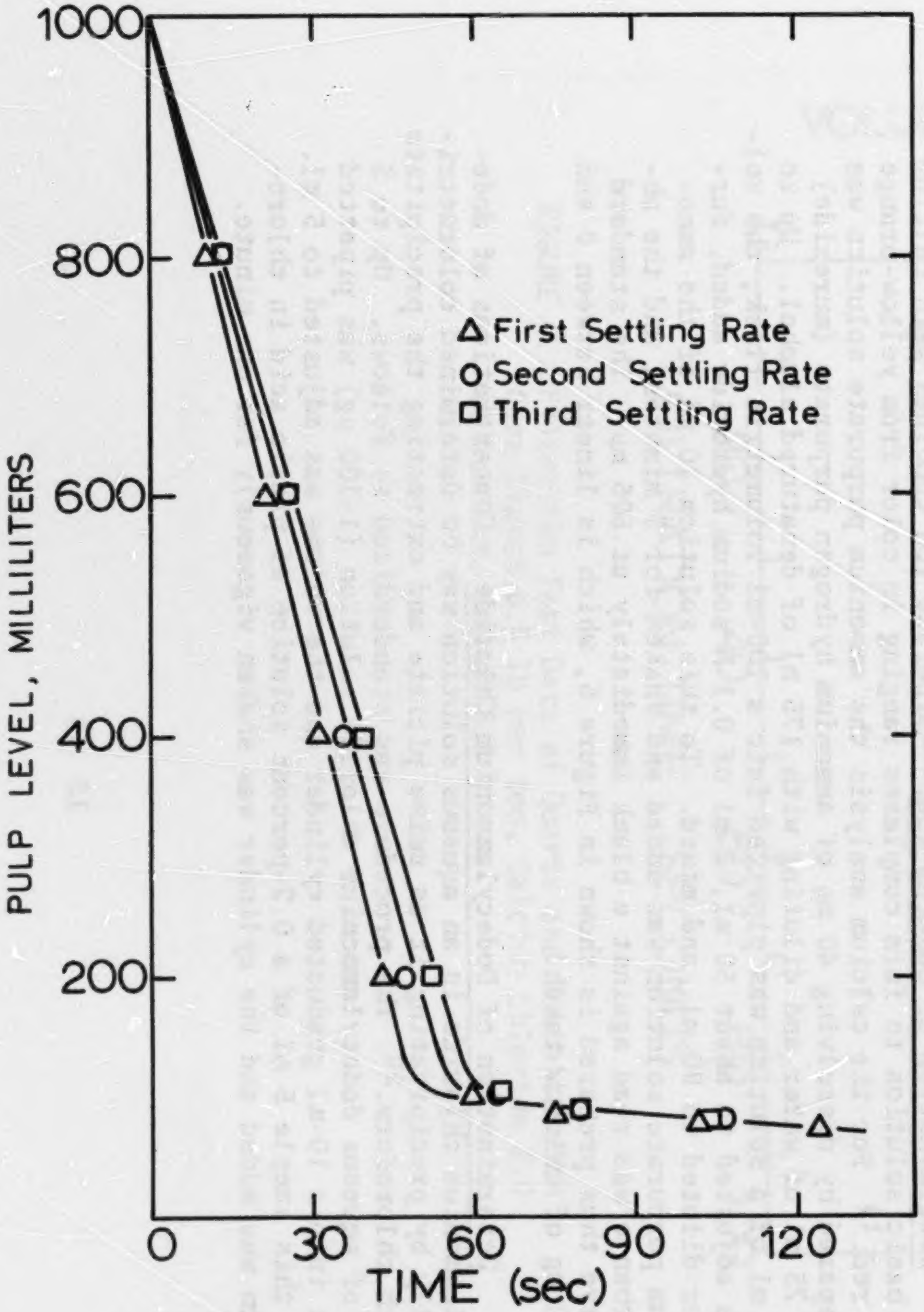


FIGURE 3(a). Settling Curves of Quartz with Corn Starch 0.09 lb/ton, Calcium Chloride 3.65 lb/ton, and pH 11.55

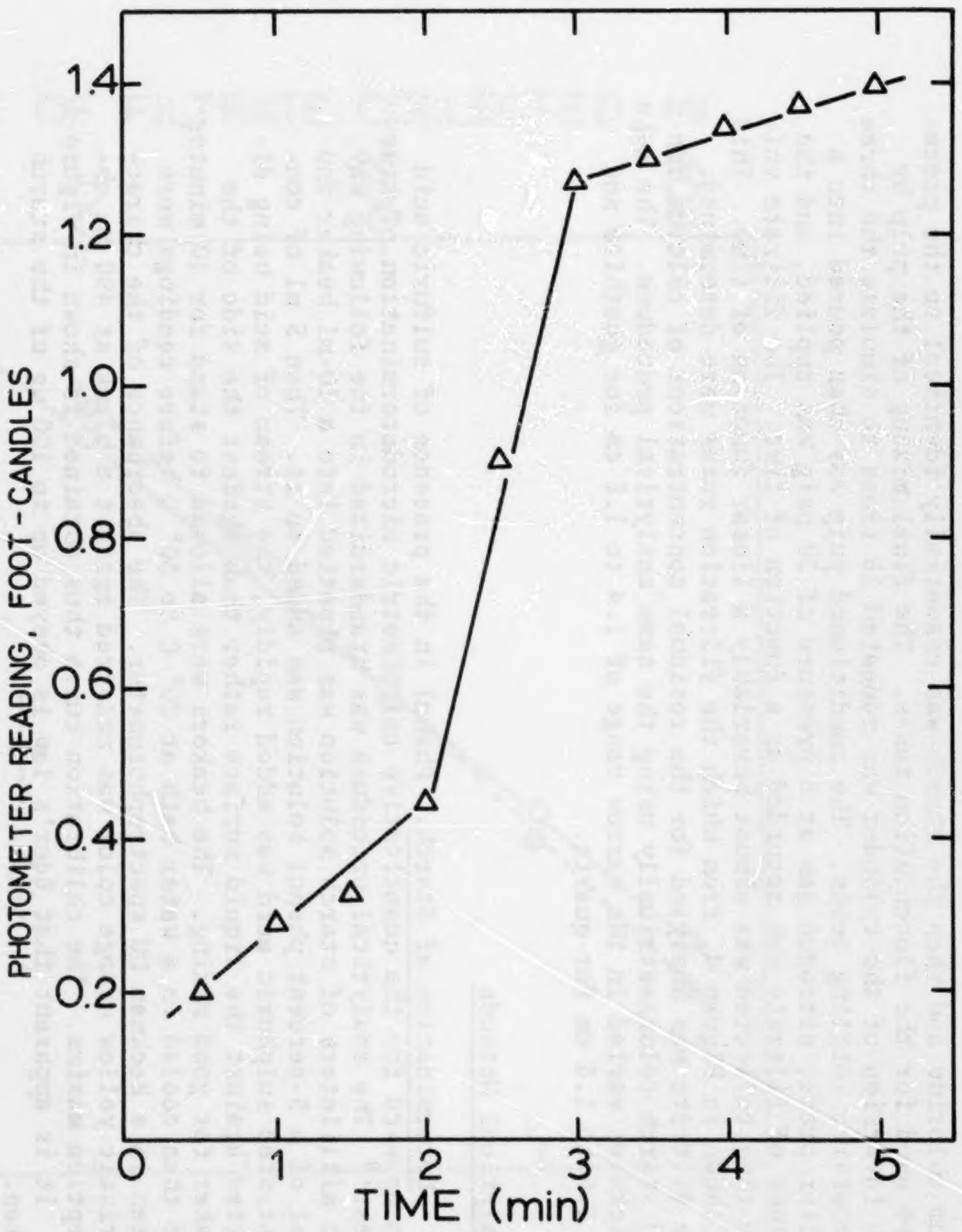


FIGURE 3(b). Settling Curve of Quartz Using a Photometer. Corn Starch 0.91 lb/ton, Calcium Chloride 0.35 lb/ton, and pH 7.45

cium chloride and then the starch was essentially identical to the procedure used for the flocculation tests. The final mixing of the pulp by the inversion of the cylinder was repeated 15 times to simulate the three successive settling tests. The conditioned pulp was then poured into a filter press, nitrogen gas at a pressure of 20 psig was applied, and the volume of filtrate was recorded as a function of time. The filtrate volume thus collected was almost invariably a linear function of time. This is shown in Figure 4, from which the filtration rates were determined. The filtrate was analyzed for the residual concentrations of calcium ion and starch colorimetrically using the same analytical procedure. The cake thickness varied in the narrow range of 1.4 to 1.5 cm for goethite and of 1.6 to 1.8 cm for quartz.

Analytical Methods

Determination of Starch. Phenol in the presence of sulfuric acid can be used for the quantitative colorimetric microdetermination of starches.[18] The analytical procedure was standardized in the following way. Two millileters of starch solution was pipetted into a 10-ml beaker and 1 ml of a 5-percent phenol solution was added to it. Then 5 ml of concentrated sulphuric acid was added rapidly, the stream of acid being directed against the liquid surface rather than against the side of the beaker for good mixing. The beakers were allowed to stand for 10 minutes and then cooled in a water bath at 20° C to 30° C before readings were taken in a Beckman DU spectrophotometer. The absorbance of the characteristic yellow orange color was measured against a blank at 490 mμ absorption maxima. The calibration curve thus obtained is shown in Figure 5. It is apparent that Beer's law is obeyed up to 100 μg of the starch taken.

Determination of Calcium Ion. Purpurate ion combines with calcium in basic solution to form complexes ranging in color from yellow-orange to red.[19] For the calcium analysis the ammonium purpurate solution was prepared by dissolving 40 mg of ammonium hydrogen purpurate (murexide) in 75 ml of water and diluting with 175 ml of denatured alcohol. Up to 50 ml of a solution was pipetted into a 100-ml volumetric flask, the volume adjusted to about 50 ml, 2 ml of 0.1 N sodium hydroxide added, further diluted to 90 ml, and mixed. To this solution 10 ml of the ammonium purpurate solution was added and shaken for 5 minutes, and the absorbance was read against a blank immediately at 506 mμ. The standard curve thus prepared is shown in Figure 6, which is linear between 0 and 0.2 mg of calcium taken.

Determination of Dodecylammonium Chloride. Concentrations of dodecylammonium chloride in an aqueous solution may be determined colormetrically by precipitating it as amine picrate and extracting the precipitate with chloroform.[20] The procedure was standardized as follows. Up to 5 ml of aqueous dodecylammonium chloride solution (1-100 μg) was pipetted out into a 10-ml graduated cylinder and the volume was adjusted to 5 ml. To this sample 5 ml of a 0.2-percent solution of picric acid in chloroform was added and the cylinder was shaken vigorously for one minute.

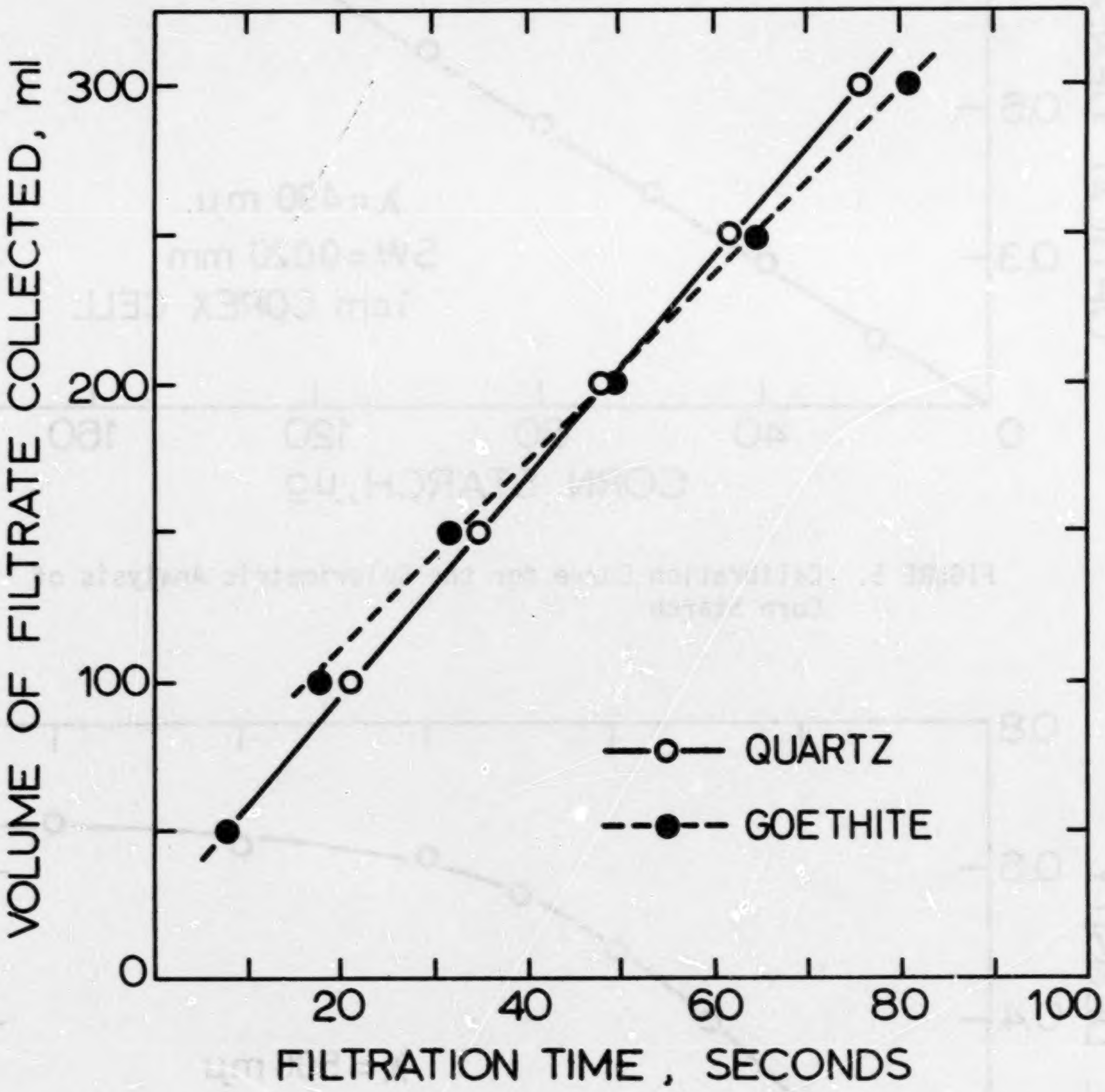


FIGURE 4. Filtration Test Data of Quartz and Goethite with Corn Starch 0.5 lb per ton, Calcium Chloride 2.0 lb per ton, and pH 9.5

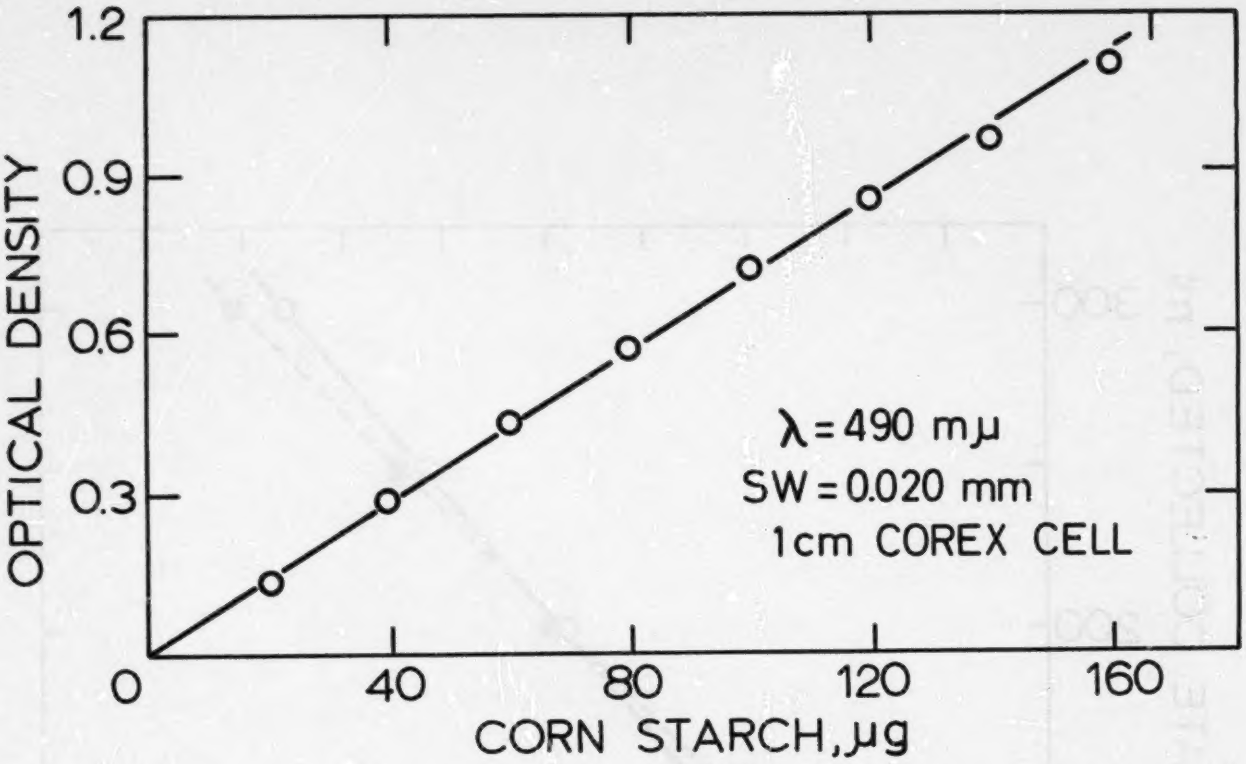


FIGURE 5. Calibration Curve for the Colorimetric Analysis of Corn Starch

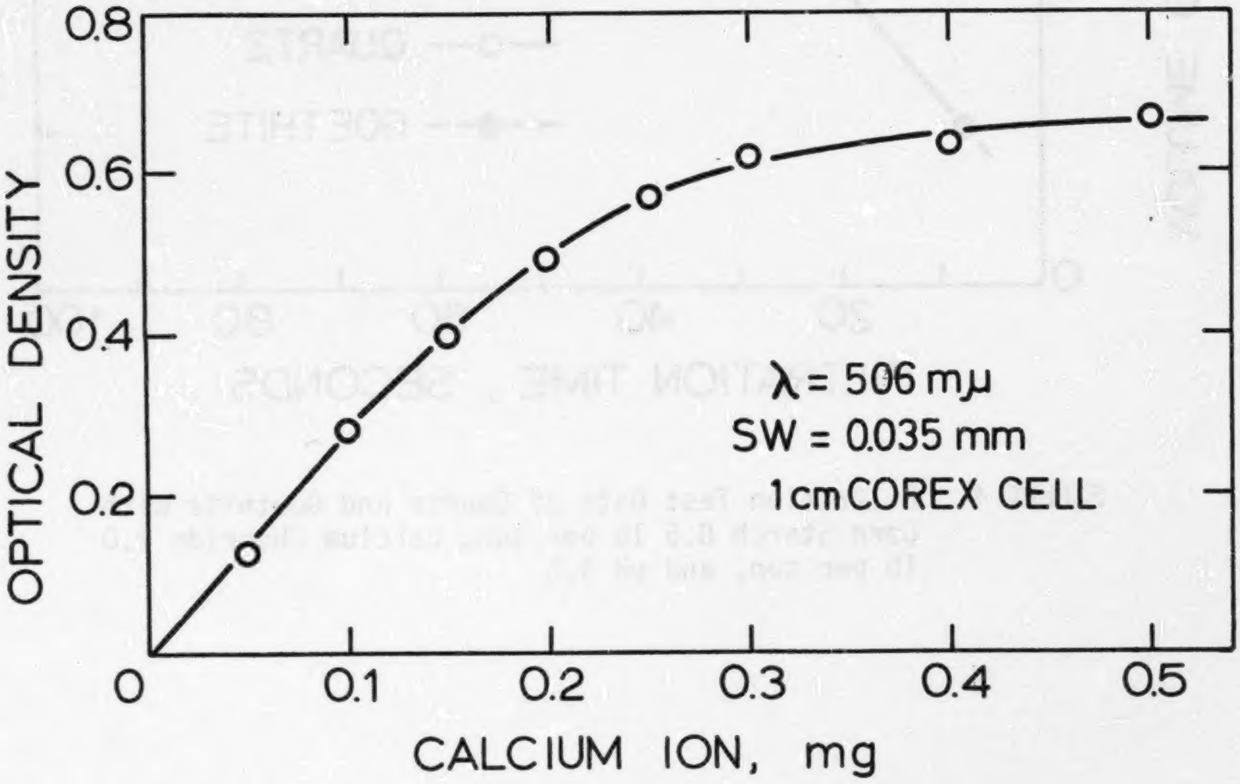


FIGURE 6. Calibration Curve for the Colorimetric Analysis of Calcium Ion

The two phases separated out on one to two hours standing. The chloroform layer was pipetted out and the absorbance was determined against a blank at 410 mμ. The standard curve, shown in Figure 7, follows Beer's law up to 100 μg of the amine taken.

Zeta-Potential Measurements

The electrokinetic behaviors of quartz and goethite in aqueous solutions were investigated mainly by the streaming-potential measurement technique, but electrophoretic mobility measurements were also used to check the behavior of ground quartz samples.

Streaming-Potential Measurements were made by forcing a liquid through a porous plug of mineral particles under known applied pressure and measuring the potential difference generated across the plug. The zeta potential was calculated according to the Helmholtz-Smoluchowski equation

$$\zeta = \frac{4\pi\eta}{\varepsilon} \cdot \frac{\lambda E}{P}$$

where ζ is the zeta potential, η is the viscosity, ε is the dielectric constant, λ is the specific conductance of the solution, E is the potential difference, and P is the applied pressure. The cell assembly was similar to that described by Fuerstenau,[21] and is schematically shown in Figure 8(a). The streaming potential was measured with a Hewlett-Packard Model 412A DC vacuum tube voltmeter together with a Leeds and Northrup Speedmax AZAR recorder, and the specific conductance was determined by measuring the resistance of the plug *in situ* with an Electromeasurements Model 250 Impedance Bridge.

The effect of pressure on the streaming potential developed across a goethite plug was investigated in a solution containing 50 mg of corn starch per liter. The results, plotted in Figure 8(b) agree with the theory that the ratio E/P is a constant and is independent of the direction of liquid flow.

Electrophoretic Mobility Measurements. A flat type, vertical, microelectrophoresis cell, having dimensions of 40 mm in length, 18 mm in height, and 2.46 mm in width, was used with a petrographic microscope. A rectangular cell containing a dilute copper sulfate solution was inserted between the light source and the microscope to minimize convection due to heating in the cell. Two pieces of No. 22 gauge platinum wire were used as electrodes. The experimental set-up is shown schematically in Figure 9. The microscope was focused at the zero velocity layer of the liquid corresponding to 21.2 percent of the inner width of the cell.[1] The cell was filled with a conditioned suspension, and a potential of 22.5 volts was applied, and the rate of motion of particles was determined by measuring the time in seconds required to travel a given distance. The polarity of electrodes was then reversed, the rate of particle motion was determined in the reverse direction, and the two val-

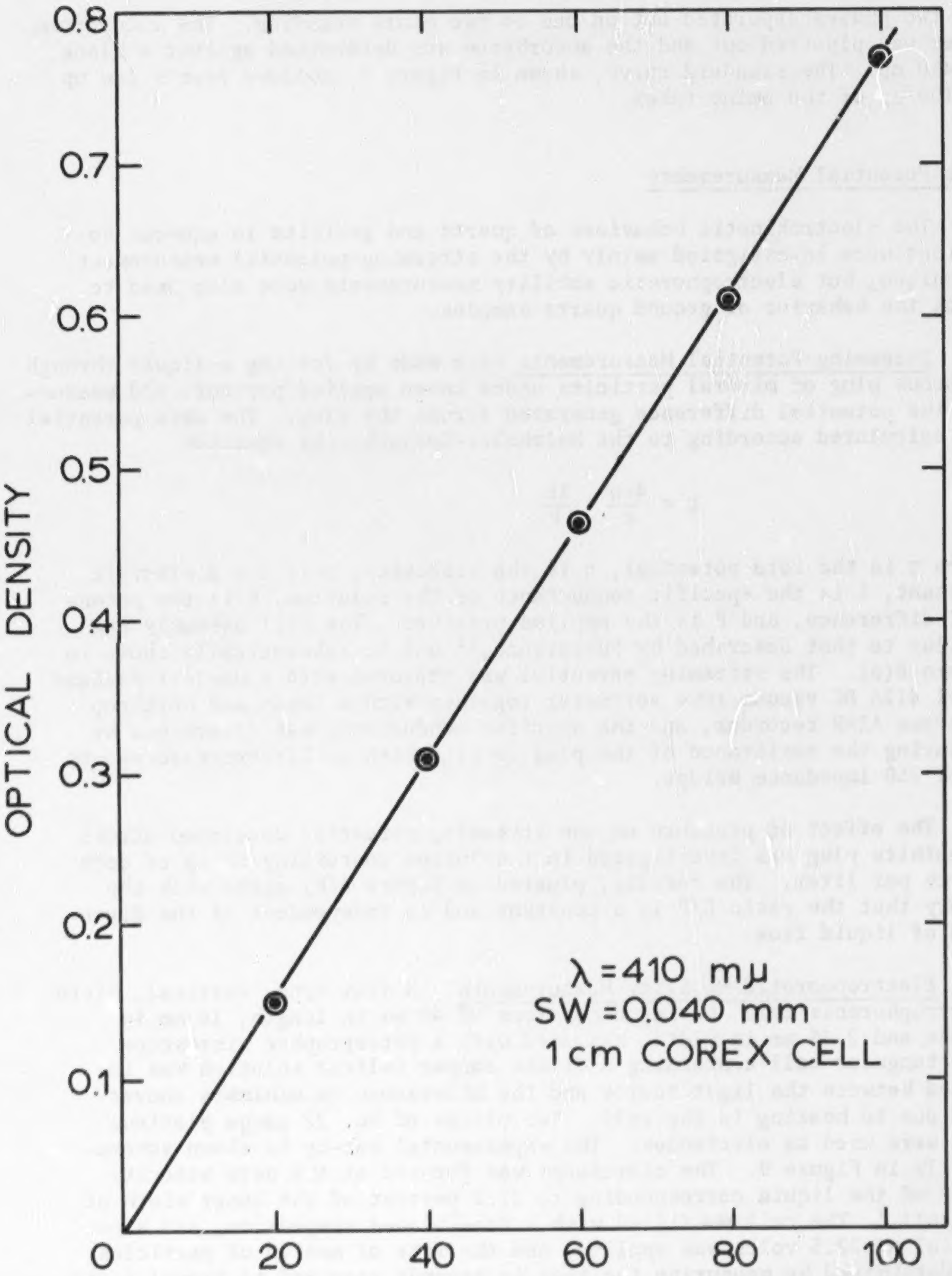


FIGURE 7. Calibration Curve for the Colorimetric Analysis of Dodecylammonium Chloride

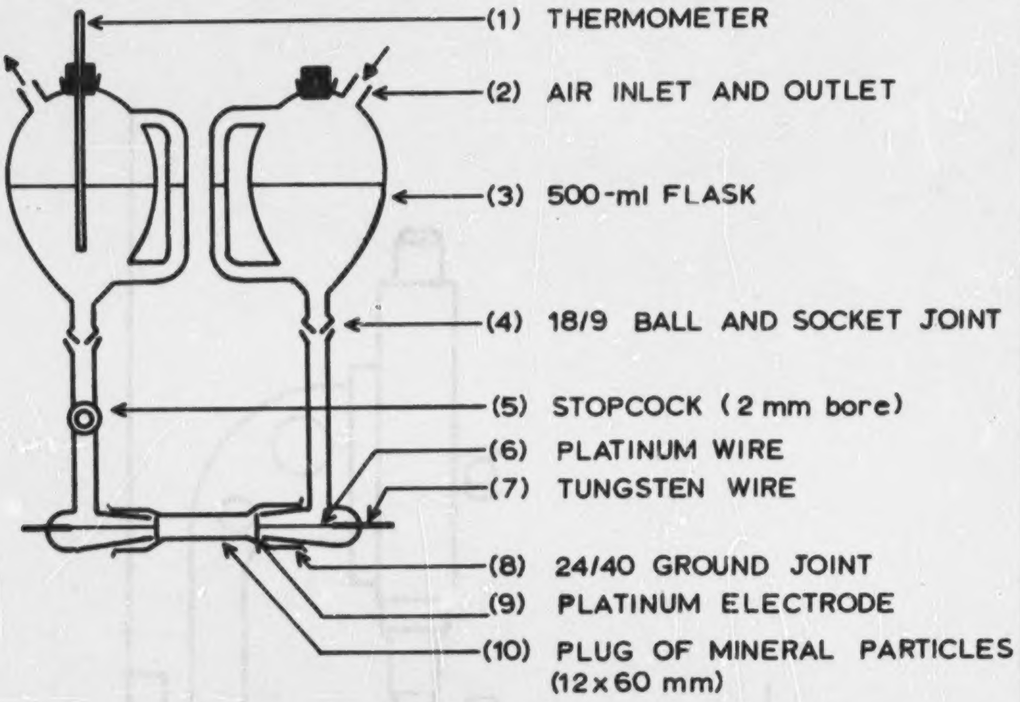

(1) THERMOMETER
(2) AIR INLET AND OUTLET
(3) 500-ml FLASK
(4) 18/9 BALL AND SOCKET JOINT
(5) STOPCOCK (2 mm bore)
(6) PLATINUM WIRE
(7) TUNGSTEN WIRE
(8) 24/40 GROUND JOINT
(9) PLATINUM ELECTRODE
(10) PLUG OF MINERAL PARTICLES (12x60 mm)

FIGURE 8(a). Schematic Diagram of Streaming-Potential Cell

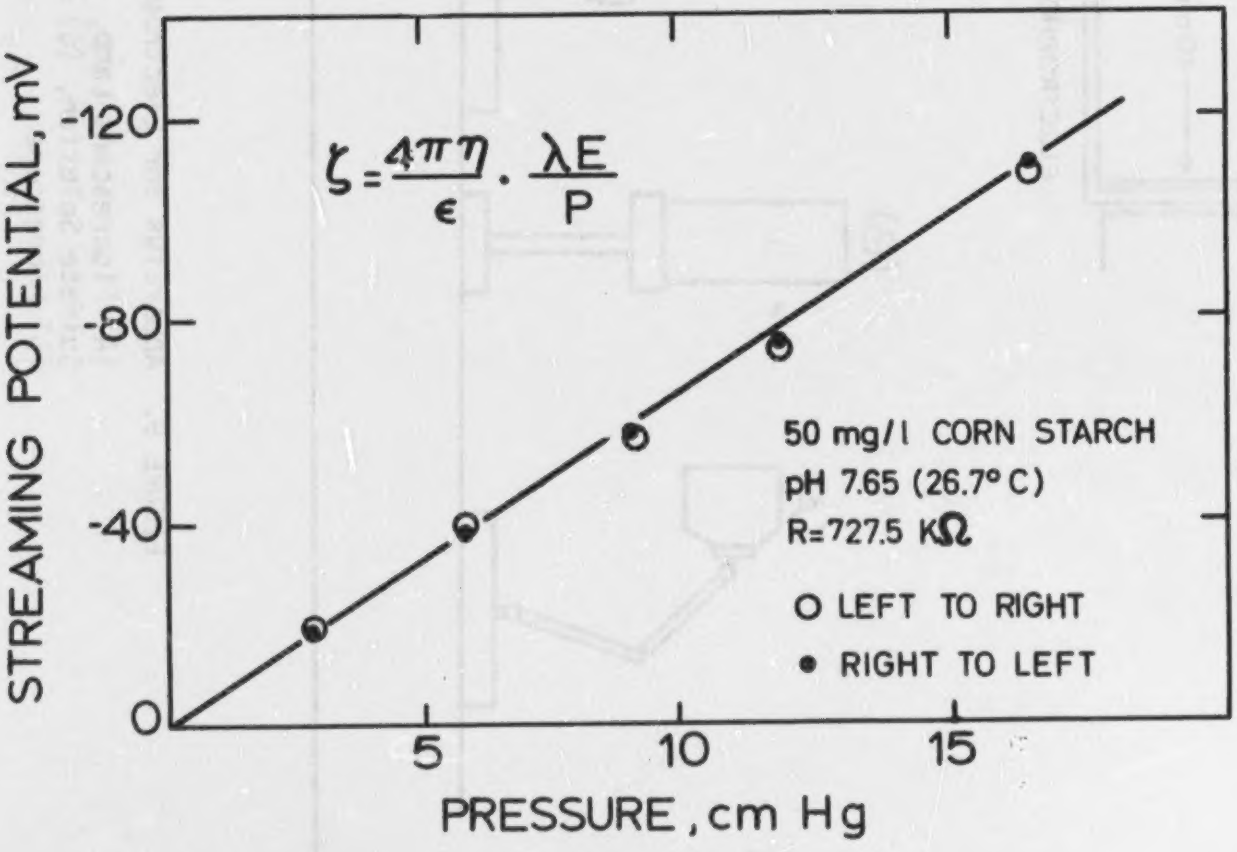


FIGURE 8(b). Streaming Potential of Goethite as a Function of Pressure

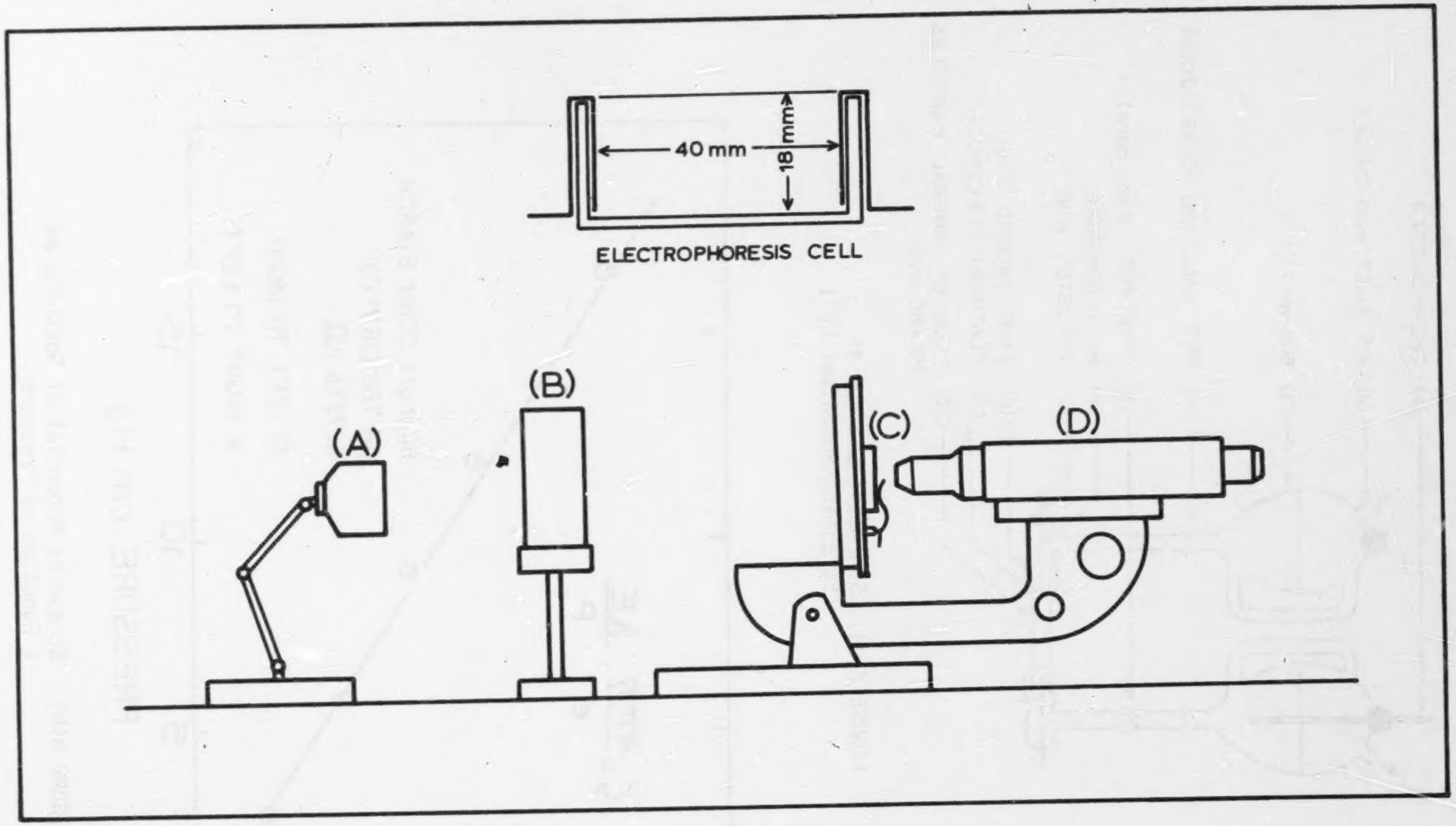

40 mm
18 mm
ELECTROPHORESIS CELL
(A)
(B)
(C)
(D)

FIGURE 9. Apparatus for Electrophoresis Mobility Measurements

(A) Fluorescent Lamp, (B) Cell Filled with Copper Sulfate Solution, (C) Electrophoresis Cell, and (D) Microscope ues were averaged. The observations were repeated until ten pairs of the readings were obtained, and with the harmonic average and the values of applied potential the electrophoretic mobility was calculated from the equation

$$u\,(\text{cm/sec/volt/cm}) = \frac{\text{Path length (cm)} \times \text{Distance between electrodes (cm)}}{\text{Time (sec)} \times \text{Potential difference in cell (volts)}}$$

Though the value of zeta potentials evaluated from the electrophoretic mobility data is mentioned to be open to serious doubt due to the relaxation correction,[22] the data are often converted to zeta potentials using the von Smoluchowski equation

$$\zeta = \frac{4\pi\eta}{\varepsilon} u$$

Restrictions imposed on this equation are that the double layer must be thin as compared to the particle size and that the surface conductance is negligible. Another expression for the electrophoretic mobility was given by Hückel on an ion surrounded by an ionic atmosphere as follows.

$$\zeta = \frac{6\pi\eta}{\varepsilon} u$$

Colloid particles exhibit some intermediate values with a numerical factor dependent upon the particle size and the reciprocal thickness of the double layer.

Viscosity Measurements. A Cannon-Fenske capillary viscometer No. 50 immersed in a Sargent thermistor-controlled oil bath was used for the measurements. A self-levelling viscometer clamp was used to suspend the viscometer in the bath. All viscosity measurements were made at 25° C, the equipment controlling the temperature to within 0.1° C. From a few preliminary tests the starch concentration was fixed at 0.4 percent for all the measurements. The efflux times for the sample solution (t_s) and solvent (t_o) thus determined were then converted to the relative viscosities according to[23]

$$\eta_r = t_s/t_o$$

SECTION VI

EXPERIMENTAL RESULTS

Flocculation Behavior With Starches

Effect of Corn Starch, Calcium Chloride, and pH

Flocculation Tests on Quartz. To investigate the effects of the three major variables on the flocculation behavior of a quartz suspension, a three-factor orthogonal composite design was used. From a few preliminary tests the ranges of the three variables were selected as shown in Table 1. The quartz sample used in this series of tests was that ground for 120 minutes, having a size modulus of 60 microns. The results of the settling rates, the suspended solids, the residual starch, and calcium ion concentrations are given in Columns Y_1, Y_2, Y_3, and Y_4, respectively, in the same table.

The experimental points were fitted with second-order equations by the method of least squares. The regression equations thus generated were as follows:

$$\begin{aligned}\text{(Settling Rate)} = {} & 3.73 - 1.20X_1 + 1.99X_2 + 2.14X_3 + 0.64X_1^2 \\ & + 0.03X_2^2 + 2.80X_3^2 + 0.81X_1X_2 - 1.16X_1X_3 \\ & + 0.82X_2X_3; \quad r = 0.93 \quad (\phi = 10)\end{aligned} \qquad [1]$$

$$\begin{aligned}\text{(Suspended Solids)} = {} & 2559 + 1020X_1 - 1401X_2 + 223X_3 - 421X_1^2 \\ & + 825X_2^2 - 123X_3^2 - 818X_1X_2 + 341X_1X_3 \\ & - 409X_2X_3; \quad r = 0.93 \quad (\phi = 10)\end{aligned} \qquad [2]$$

$$\begin{aligned}\text{(Starch Concentration)} = {} & 8.35 + 6.81X_1 - 1.61X_2 + 0.54X_3 \\ & - 0.39X_1^2 + 0.63X_2^2 - 0.90X_3^2 \\ & - 0.93X_1X_2 + 0.95X_1X_3 - 0.69X_2X_3; \\ & r = 1.0 \quad (\phi = 10)\end{aligned} \qquad [3]$$

$$\begin{aligned}\text{(Calcium Concentration)} = {} & 15.25 + 0.15X_1 + 14.76X_2 - 2.26X_3 \\ & + 0.04X_1^2 + 1.75X_2^2 - 0.63X_3^2 \\ & + 0.05X_1X_2 - 0.21X_1X_3 - 1.84X_2X_3; \\ & r = 1.0 \quad (\phi = 10)\end{aligned} \qquad [4]$$

where X_1 = starch addition (lb per ton)
X_2 = calcium chloride addition (lb per ton)
X_3 = pH

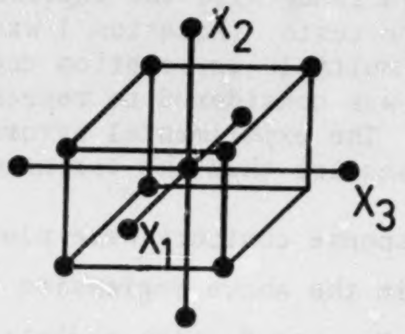
TABLE 1. COMPOSITE DESIGN AND PRODUCT DATA FOR FLOCCULATION TESTS ON QUARTZ

Factors:

X_1 = Corn Starch, pound per ton
X_2 = Calcium Chloride, pound per ton
X_3 = pH

Responses:

Y_1 = Settling Rate, inch per minute
Y_2 = Suspended Solids in supernate, ppm
Y_3 = Residual Starch Concentration, ppm
Y_4 = Residual Calcium Concentration, ppm



Design Levels			Factor Levels			Responses			
X_1	X_2	X_3	X_1	X_2	X_3	Y_1	Y_2	Y_3	Y_4
-1	-1	-1	0.09	0.35	7.45	5.31	960	1	2.5
1	-1	-1	0.91	0.35	7.45	3.06	2570	13	3
-1	1	-1	0.09	3.65	7.45	5.79	570	1	38
1	1	-1	0.91	3.65	7.45	5.54	1130	12	38
-1	-1	1	0.09	0.35	11.55	10.5	1230	1	1
1	-1	1	0.91	0.35	11.55	2.31	6010	20	1.5
-1	1	1	0.09	3.65	11.55	14.1	680	0	27
1	1	1	0.91	3.65	11.55	11.0	680	12	27
-1.215	0	0	0.0	2.0	9.5	2.38	670	0	16
1.215	0	0	1.0	2.0	9.5	5.19	3510	15	13
0	-1.215	0	0.5	0.0	9.5	0*	7120	12	0
0	1.215	0	0.5	4.0	9.5	5.75	740	6	34
0	0	-1.215	0.5	2.0	7.0	4.60	970	7	14
0	0	1.215	0.5	2.0	12.0	9.40	800	6.5	13
0	0	0	0.5	2.0	9.5	5.37	2440	10	16
1	-1	-1	0.91	0.35	7.45	3.25	4230	16	2.5
-1	1	-1	0.09	3.65	7.45	6.84	560	1	32
-1	-1	1	0.09	0.35	11.55	11.0	1070	2	0
1	1	1	0.91	3.65	11.55	10.3	620	14	27
0	0	0	0.5	2.0	9.5	4.80	2200	7.5	17
-1.215	0	0	0.0	2.0	9.5	2.34	1010	0	16

*Flocculation not apparent and settling rate of zero assigned arbitrarily.

r = multiple correlation coefficient

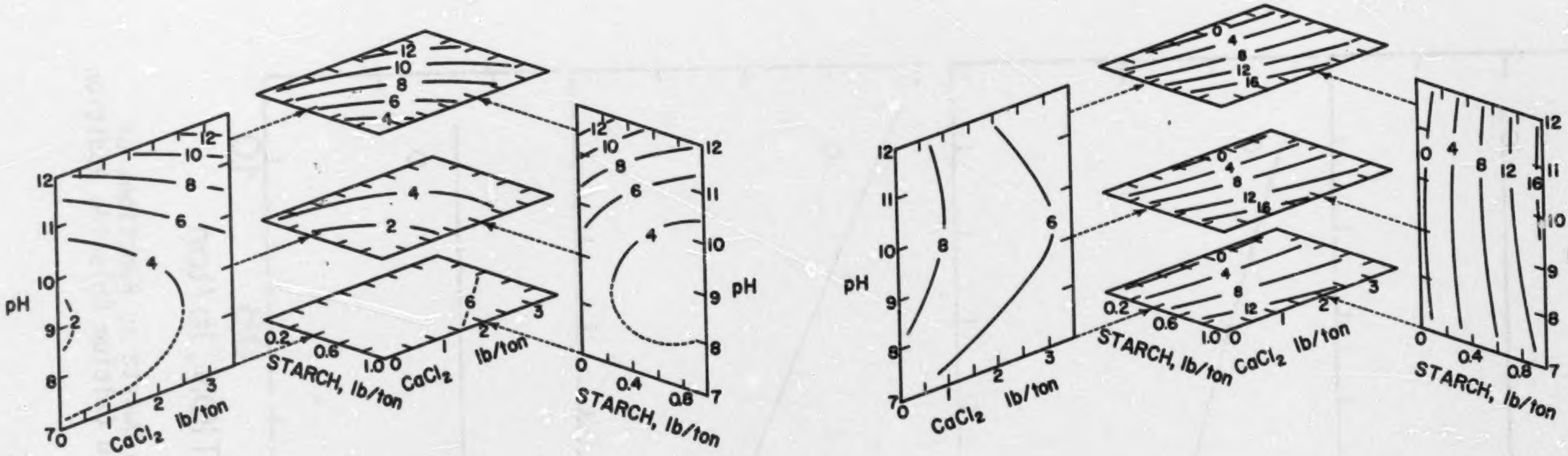
ϕ = degrees of freedom

Using an F-test, all the equations were tested by comparing the lack of fit variance with the experimental error variance, estimated for the duplicate tests. Equation 1 was found to be statistically significant, but the multiple correlation coefficient was high enough so that the equation was considered to represent the experimental results satisfactorily. The experimental errors in all the other equations were considerably smaller than the variances due to the lack of fit of the equations.

Response contours were plotted by substituting values for X_1, X_2, and X_3 in the above regression equations and solving for the responses Y_1, Y_2, Y_3, and Y_4 with a digital computer. The results are plotted in Figure 10. As seen in Figures 10(a) and 10(b) the settling rate and the amount of suspended solids are complexly dependent on all three of the variables under investigation. It is apparent in Figure 10(c) that the abstraction of starch by quartz is influenced by the calcium-ion concentration, but is relatively independent of pH in the presence of calcium ion in solution. The abstraction of calcium ion, however, is affected by the pH, whereas it is virtually independent of the starch concentration, as seen in Figure 10(d). This observation is in good agreement with the adsorption studies reported previously.[6,15]

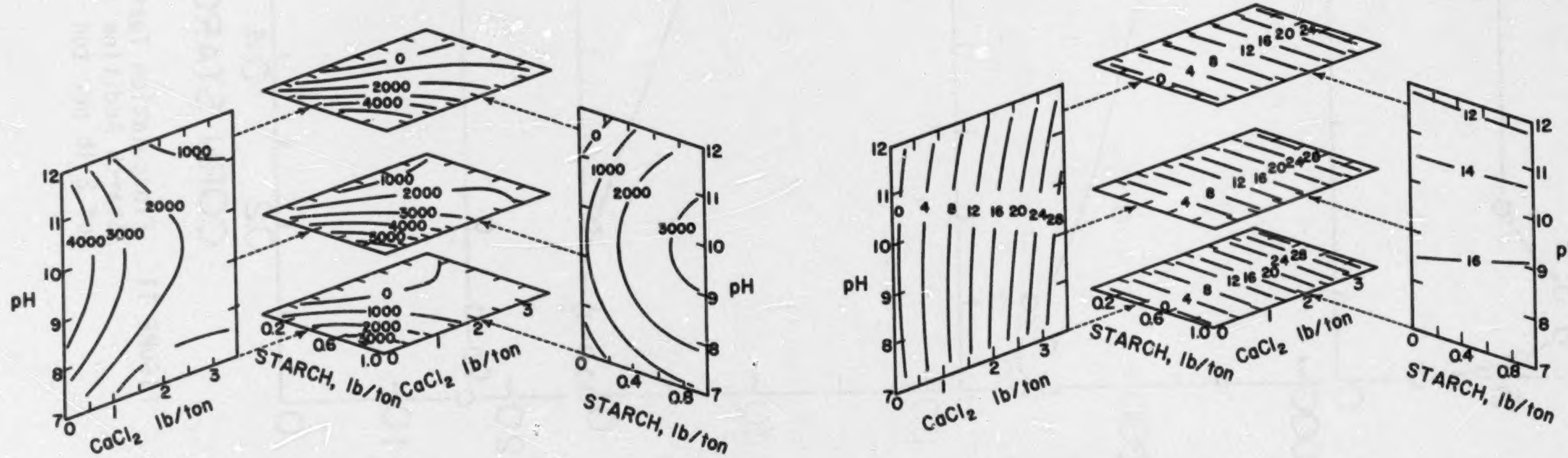
The flocculation and clarification behaviors of quartz suspensions may be more closely related to the calcium-ion concentration and the pH, and the increase in these two parameters may be fulfilled most economically through the use of lime. There appears to be a tendency in Figures 10(a) and 10(b) for both the settling rate and the clarification of the supernatant water to be impaired by the addition of starch. In the presence of a measurable excess concentration of starch a mineral suspension may be redispersed due to its protective action.

In order to substantiate the above hypothesis a number of tests were performed with various amounts of starch, particularly in the low range, but keeping all the other variables constant. From the results in Figure 10 the pH was fixed at 9.5 and the level of calcium chloride addition at 2 pounds per ton. This level of addition resulted in a residual calcium-ion concentration of 15 to 18 ppm, a typical value of Minneapolis tap water. The test results, which are shown graphically in Figure 11, indicate that, as the amount of starch is increased, the settling rate increases initially reaching a maximum at about 0.075 pound per ton, and then decreases to a constant rate at about 0.2 pound per ton. The amount of the suspended solids appears to undergo a minimum in the neighborhood of the starch level where the settling rate is at a maximum. The residual starch concentration is a trace as shown in the figure. Beyond 0.1 pound of starch per ton a measurable quantity of starch, in excess of several ppm, appears in the solution, the settling rate remains constant, and the amount of suspended solids increases with the starch addition. As expected, the residual calcium-ion concentration remains nearly con-



(a) SETTLING RATE, inch/min.

(c) RESIDUAL STARCH CONC., ppm



(b) SUSPENDED SOLID, ppm

(d) RESIDUAL CALCIUM ION CONC., ppm

FIGURE 10. Response Contours of Quartz Flocculation Tests Settling rate (a), Suspended Solids Concentration in Supernate (b), Residual Starch Concentration (c), and Residual Calcium-ion Concentration (d), as Functions of pH, Calcium Chloride, and Starch

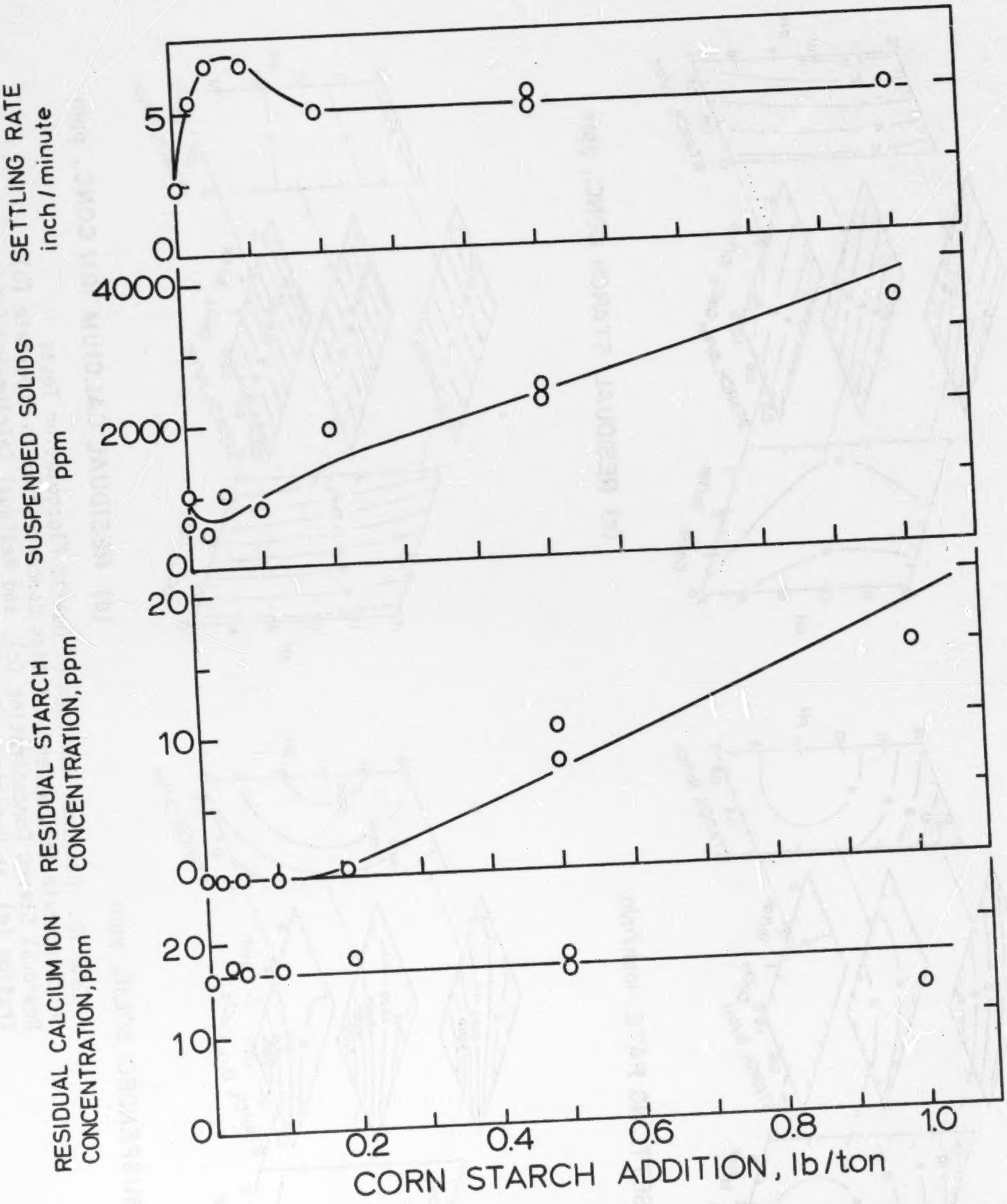


FIGURE 11. Flocculation Test Results on Quartz as Functions of Starch Addition at pH 9.5 and Calcium Chloride Addition of 2 lb per ton

stant throughout the tests. The response contours shown in Figure 10 are in good agreement with the test results, except that the contours fail to indicate the presence of a maximum in the settling rate due presumably to the lack of a sufficient number of experimental points within this range. Figure 12 shows the effect of pH under otherwise identical test conditions. The settling rates are seen to be strongly dependent on pH; the higher the pH, the higher the settling rate again in good agreement with the results presented in Figure 10. The starch level where the settling rate is at a maximum at pH 11 is seen to be located near that at pH 9.5. At pH 4 the maximum that was observed at the other two pH is not observed. It appears that the decreased adsorption of calcium ion at low pH resulted in the decreased adsorption of starch and the condition corresponding to protective action is not realized at this adsorption density.

It then became of interest to perform a three-factor orthogonal composite experiment in which the starch level ranged from 0 to 0.1 pound per ton. After the experiment had been carried out, the experimental points were fitted with second-order equations by the method of least squares and the equations were plotted graphically.

The results of the above experiment are presented in Table 2 and the graphs of the equations are shown as before in Figures 13(a), (b), (c), and (d). The contours of the residual starch concentrations are not shown since virutally all the starch added had been abstracted by the quartz sample. The settling rates at the three levels of pH are seen to depend very strongly on the level of starch addition, and, as expected, the settling rates increase with an increase in the starch level. It is also noted that the settling rates increase as the pH is raised, but are virtually independent of the level of calcium chloride addition. The amounts of suspended solids are seen to depend more strongly on the calcium chloride level than the other parameters. By comparing the contour lines of Figures 13(b) and (d) it is apparent that a close correlation exists between the amount of suspended solids and the residual calcium-ion concentration. This particular point will be discussed in great detail together with the results of the streaming-potential measurements later in Section VII.

It is noted in Figures 10 through 13 that the amount of suspended solids even at the lowest level was in excess of 500 ppm and that the supernatant solution appeared turbid. It is well known[24] that quartz suspended, particularly in an alkaline medium, is extremely difficult to flocculate with a synthetic polymer. In fact, it has been mentioned that silica particles in water might act as a hydrophilic colloid.[25]

Flocculation Tests on Goethite. To investigate the effect of the same three variables on the flocculation of goethite suspensions, an identical procedure was used. The design levels and the product data are given in Table 3, and the regression equations are shown graphically in Figures 14(a), 14 (b), and 14(d). The contours of the residual starch concentration are not shown since virtually all the starch added has been abstracted by the goethite sample. The responses are seen to be quite different from those of quartz. The settling rates are strongly dependent on the level

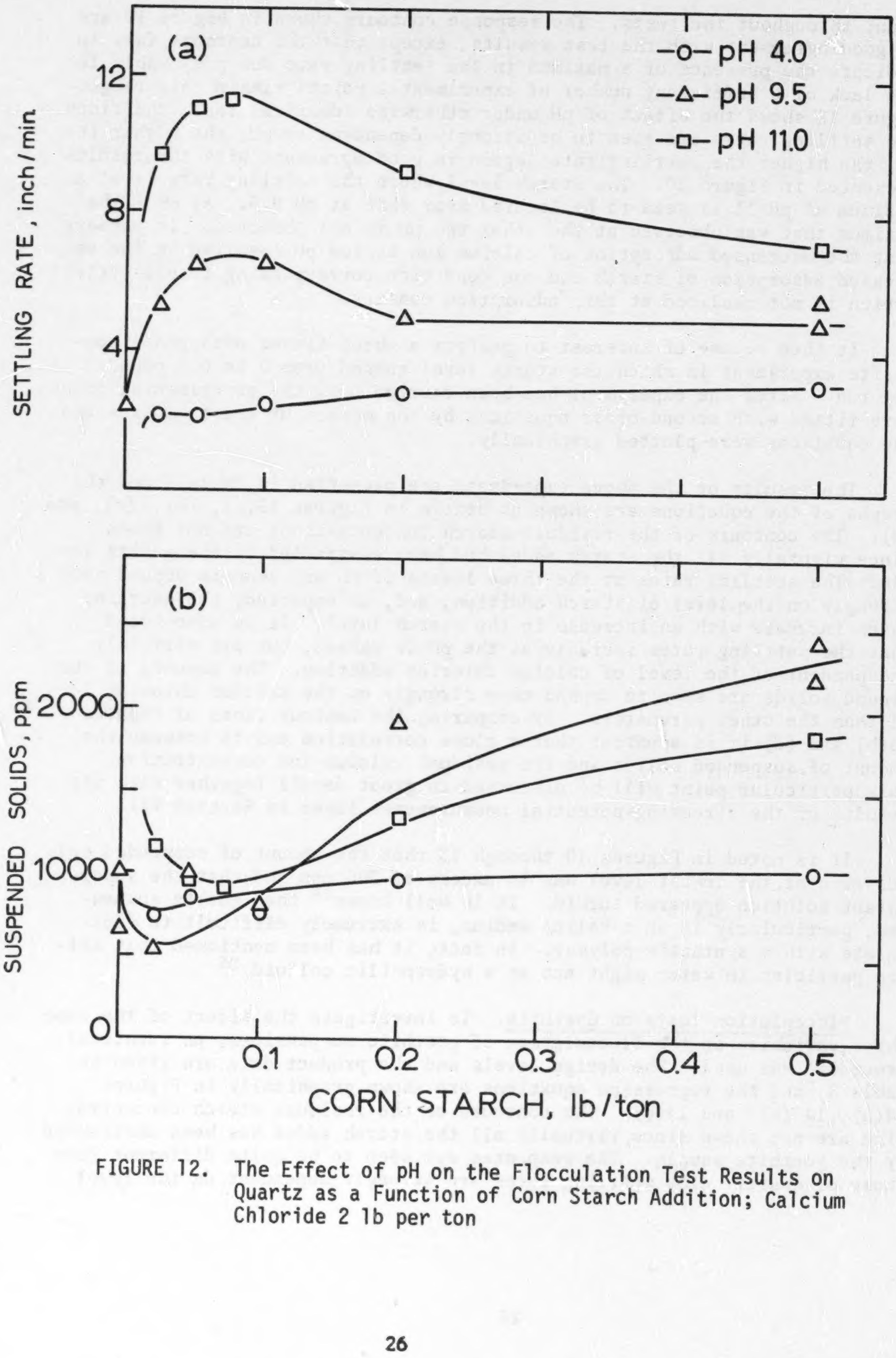
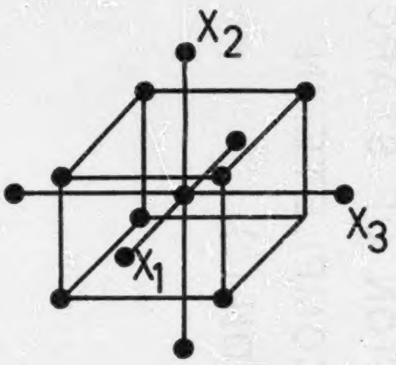


FIGURE 12. The Effect of pH on the Flocculation Test Results on Quartz as a Function of Corn Starch Addition; Calcium Chloride 2 lb per ton

TABLE 2. COMPOSITE DESIGN AND PRODUCT DATA FOR FLOCCULATION TESTS ON QUARTZ



Factors:

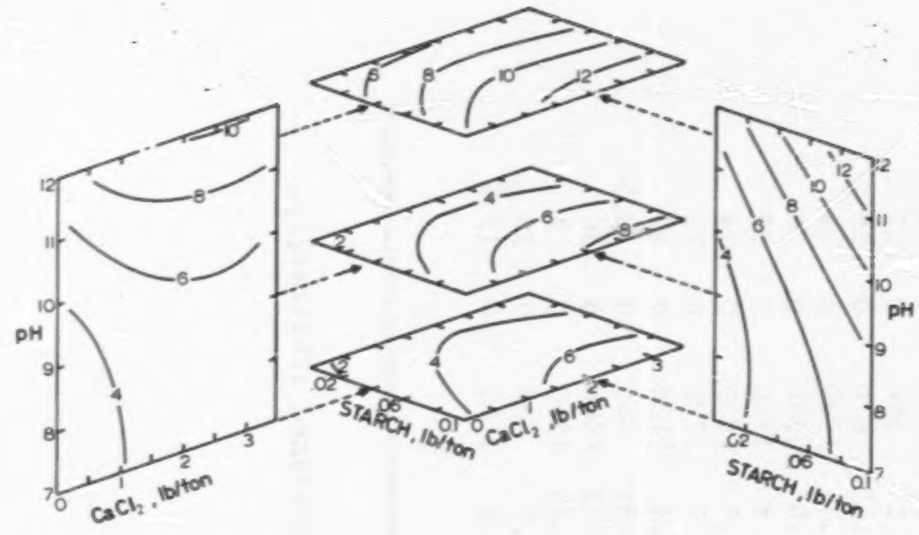
X_1 = Corn Starch, pound per ton
X_2 = Calcium Chloride, pound per ton
X_3 = pH

Responses:

Y_1 = Settling Rate, inch per minute
Y_2 = Suspended Solids in supernate, ppm
Y_3 = Residual Starch Concentration, ppm
Y_4 = Residual Calcium Concentration, ppm

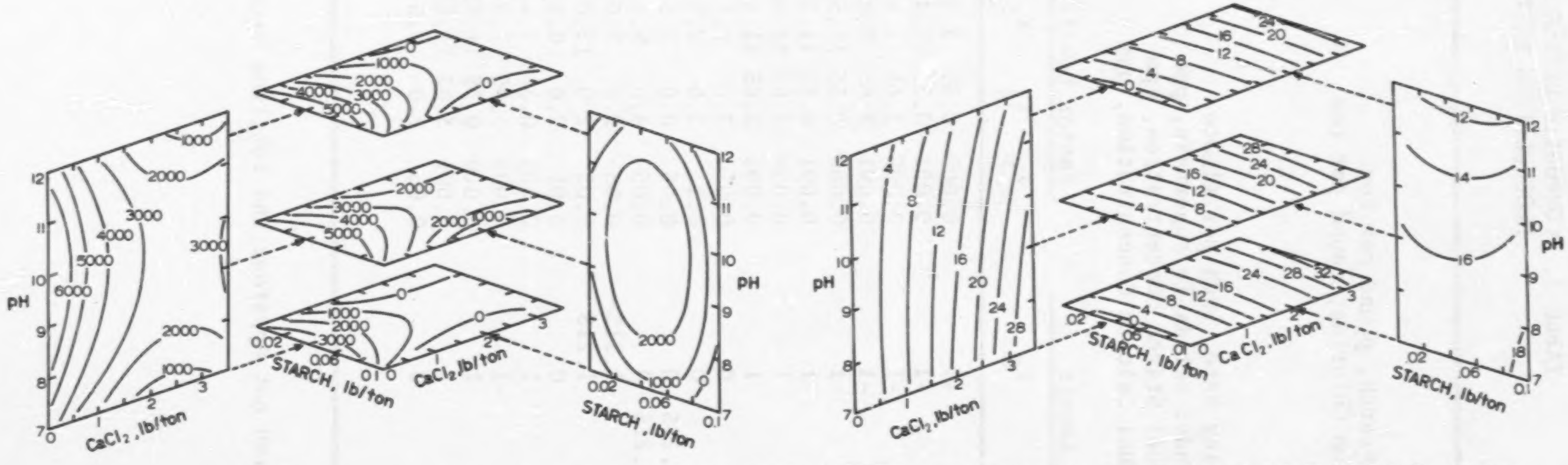
Design Levels			Factor Levels			Responses			
X_1	X_2	X_3	X_1	X_2	X_3	Y_1	Y_2	Y_3	Y_4
-1	-1	-1	0.009	0.35	7.45	3.2	1620	0	3
1	-1	-1	0.091	0.35	7.45	4.55	2180	0	3.5
-1	1	-1	0.009	3.65	7.45	2.42	1360	0	32
1	1	-1	0.091	3.65	7.45	5.79	570	0	38
-1	-1	1	0.009	0.35	11.55	6.53	4710	0	1.5
1	-1	1	0.091	0.35	11.55	10.5	1230	0	1
-1	1	1	0.009	3.65	11.55	4.66	760	0	26
1	1	1	0.091	3.65	11.55	14.1	680	0	27
-1.215	0	0	0.0	2.0	9.5	2.38	670	0	16
1.215	0	0	0.1	2.0	9.5	8.4	1740	0	14
0	-1.215	0	0.05	0.0	9.5	0.0*	10290	0	0
0	1.215	0	0.05	4.0	9.5	7.2	1760	0	32
0	0	-1.215	0.05	2.0	7.0	3.6	1800	0	14
0	0	1.215	0.05	2.0	12.0	10.7	1200	0	12
0	0	0	0.05	2.0	9.5	7.4	2150	0	17
1	-1	-1	0.091	0.35	7.45	5.31	960	0	2.5
-1	1	-1	0.009	3.65	7.45	2.52	1400	0	36
-1	-1	1	0.009	0.35	11.55	5.45	4290	0	2
1	1	1	0.091	3.65	11.55	11.0	700	0	28
0	0	0	0.05	2.0	9.5	7.8	2160	0	17.5

*Flocculation not apparent and settling rate of zero assigned arbitrarily.



ABSTRACTION OF STARCH
NEARLY COMPLETE IN
THE REGION (c)

(a) SETTLING RATE, inch/min.



(b) SUSPENDED SOLID, ppm

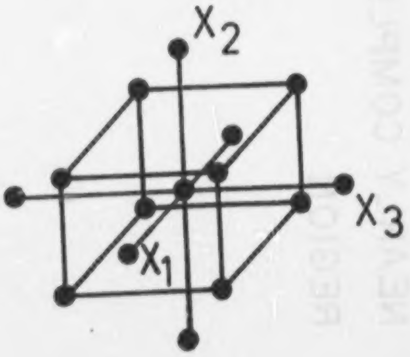
(d) RESIDUAL CALCIUM ION CONC., ppm

FIGURE 13. Response Contours of Quartz Flocculation Tests Settling Rate (a), Suspended Solids Concentration In Supernate (b), Residual Starch Concentration (c), and Residual Calcium-ion Concentration (d), as Functions of pH, Calcium Chloride, and Starch

TABLE 3. COMPOSITE DESIGN AND PRODUCT DATA FOR FLOCCULATION TESTS ON GOETHITE

Factors:

X_1 = Corn Starch, pound per ton
X_2 = Calcium Chloride, pound per ton
X_3 = pH

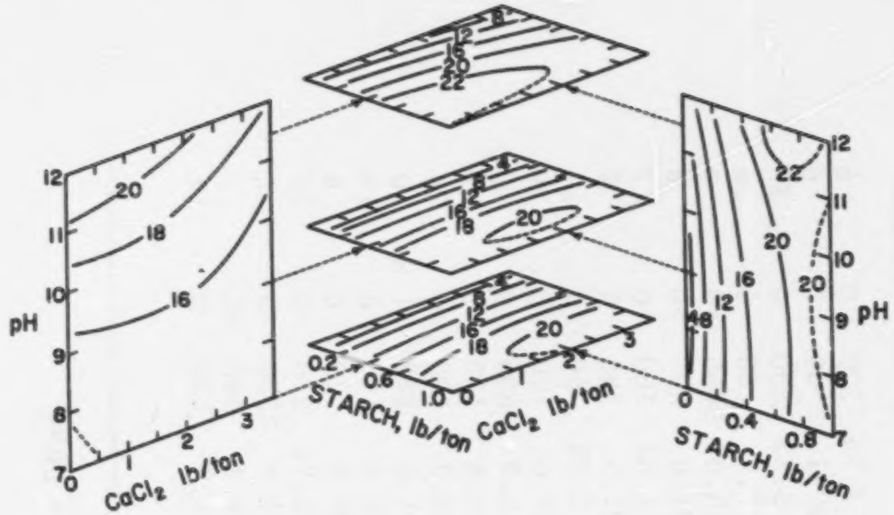


Responses:

Y_1 = Settling Rate, inch per minute
Y_2 = Suspended Solids in supernate, ppm
Y_3 = Residual Starch Concentration, ppm
Y_4 = Residual Calcium Concentration, ppm

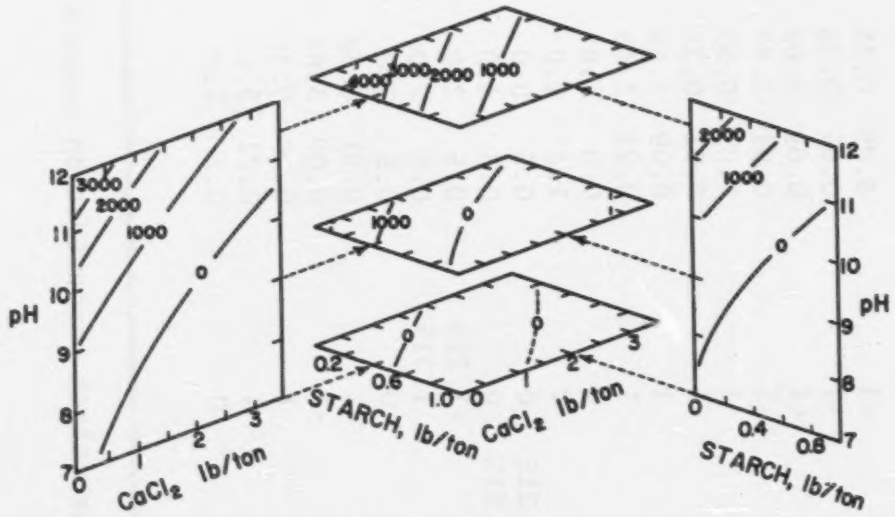
Design Levels			Factor Levels			Responses			
X_1	X_2	X_3	X_1	X_2	X_3	Y_1	Y_2	Y_3	Y_4
-1	-1	-1	0.09	0.35	7.45	3.70	220	0	6
1	-1	-1	0.91	0.35	7.45	20.1	40	0	6
-1	1	-1	0.09	3.65	7.45	5.78	200	0	39
1	1	-1	0.91	3.65	7.45	17.4	80	0	39
-1	-1	1	0.09	0.35	11.55	15.0	5480	>0	0
1	-1	1	0.91	0.35	11.55	21.0	690	>0	0
-1	1	1	0.09	3.65	11.55	5.64	360	0	7
1	1	1	0.91	3.65	11.55	21.5	380	0	7
-1.215	0	0	0.0	2.0	9.5	2.36	260	0	17
1.215	0	0	1.0	2.0	9.5	19.6	100	0	15
0	-1.215	0	0.5	0.0	9.5	15.0	600	0	0
0	1.215	0	0.5	4.0	9.5	18.8	150	0	32
0	0	-1.215	0.5	2.0	7.0	16.7	100	0	25
0	0	1.215	0.5	2.0	12.0	21.5	880	1.5	0
0	0	0	0.5	2.0	9.5	18.8	130	0	14
1	-1	-1	0.91	0.35	7.45	20.1	20	0	8
-1	1	-1	0.09	3.65	7.45	5.71	270	>0	37
-1	-1	1	0.09	0.35	11.55	14.6	4280	>0	0
1	1	1	0.91	3.65	11.55	18.8	380	>0	7
0	0	0	0.5	2.0	9.5	18.8	130	0	14

>0 indicates starch concentration somewhat higher than 0 ppm.

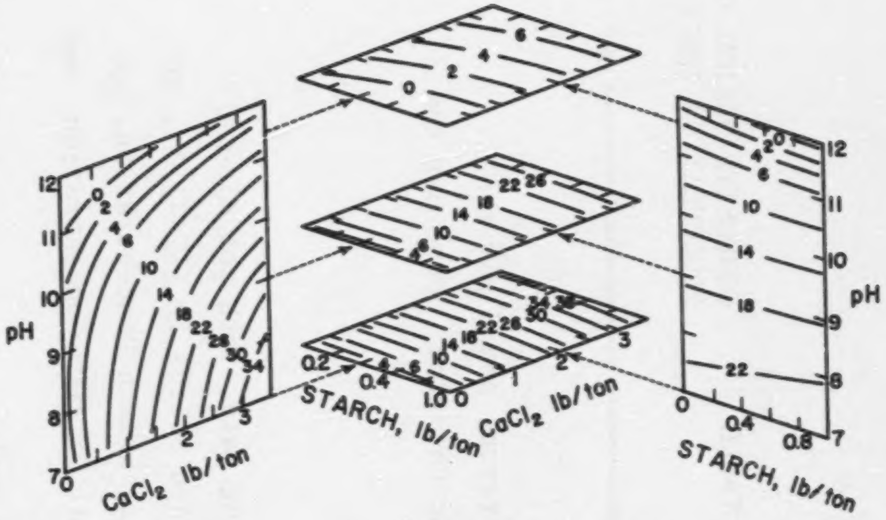


(a) SETTLING RATE, inch/min.

ABSTRACTION OF STARCH
NEARLY COMPLETE IN THE
REGION



(b) SUSPENDED SOLID, ppm



(d) RESIDUAL CALCIUM ION CONC., ppm

FIGURE 14. Response Contours of Goethite Flocculation Tests Settling Rate (a), Suspended Solids Concentration in Supernate (b), and Residual Calcium-Ion Concentration (d) as Functions of pH, Calcium Chloride and Starch

of starch addition, and, to a less extent, on pH and the level of calcium chloride addition. The clarity of the supernatant water improves as the levels of both calcium chloride and starch addition are increased, and the amount of the suspended solids is the lowest at near neutral pH. Since the isoelectric point of goethite is known to be at pH 6.7 (see Figure 39), the electrical charge on the solid particles is at minimum in the above pH region. The interaction of calcium ion and pH is apparent in Figure 14(d). The flocculation behavior described above appears to be readily interpreted in the light of the adsorption behavior[6,15] and the streaming-potential data described in Section VII.

To study the effect of an excessive addition of the starch flocculant, a series of flocculation tests was made extending the level of starch addition beyond one pound per ton, but keeping the other variables constant. The pH was fixed at 9.5 and the level of calcium chloride addition at 2 pounds per ton, concordant with the test conditions used on quartz in preparing Figure 11. The results thus obtained are presented in Figure 15. The settling rate increases initially and appears to reach a maximum at approximately 0.75 pound per ton. Beyond this point, a measurable quantity of starch, in excess of several ppm, appears in the supernatant solution, and the settling rate tends to decrease. The amount of suspended solids undergoes a minimum again at about a point where a measurable quantity of the starch appears in solution. The residual concentration of calcium ion in solution remains more or less constant throughout the range, as expected. The present observation is again in good accord with a view that an excessive amount of starch present in solution tends to hinder flocculation due to protective action although the level of the starch addition is an order of magnitude greater than that for quartz.

Filtration Tests. To investigate the factors governing the filtration as well as the flocculation behavior of quartz and goethite suspensions, a series of filtration tests was carried out on the same samples used in the flocculation tests. To facilitate the comparison, three-factor orthogonal composite experiments, identical to those used for the flocculation tests were followed. The design and the product data of the experiments for the quartz and goethite samples are given in Tables 4 and 5, respectively, from which regression equations were generated and response contours were calculated with a digital computer. The results thus obtained are given in Figures 16 and 17, respectively.

It is interesting to note that the general trend of the filtration rate contours of the quartz sample shown in Figure 16(a) are markedly similar to the settling rate and the suspended solid contours of the flocculation tests shown in Figures 10(a) and (b). The factors governing the filtration and flocculation behaviors of quartz, therefore, may be the same. The most obvious factor is the floc size, which is confirmed qualitatively in the experimental observation. Since the abstraction of both calcium ions and starch by quartz is relatively small, the residual concentrations of these two reagents are seen to be considerably higher at the corresponding levels of addition in the present case than in the flocculation tests due evidently to the higher percent solids used.

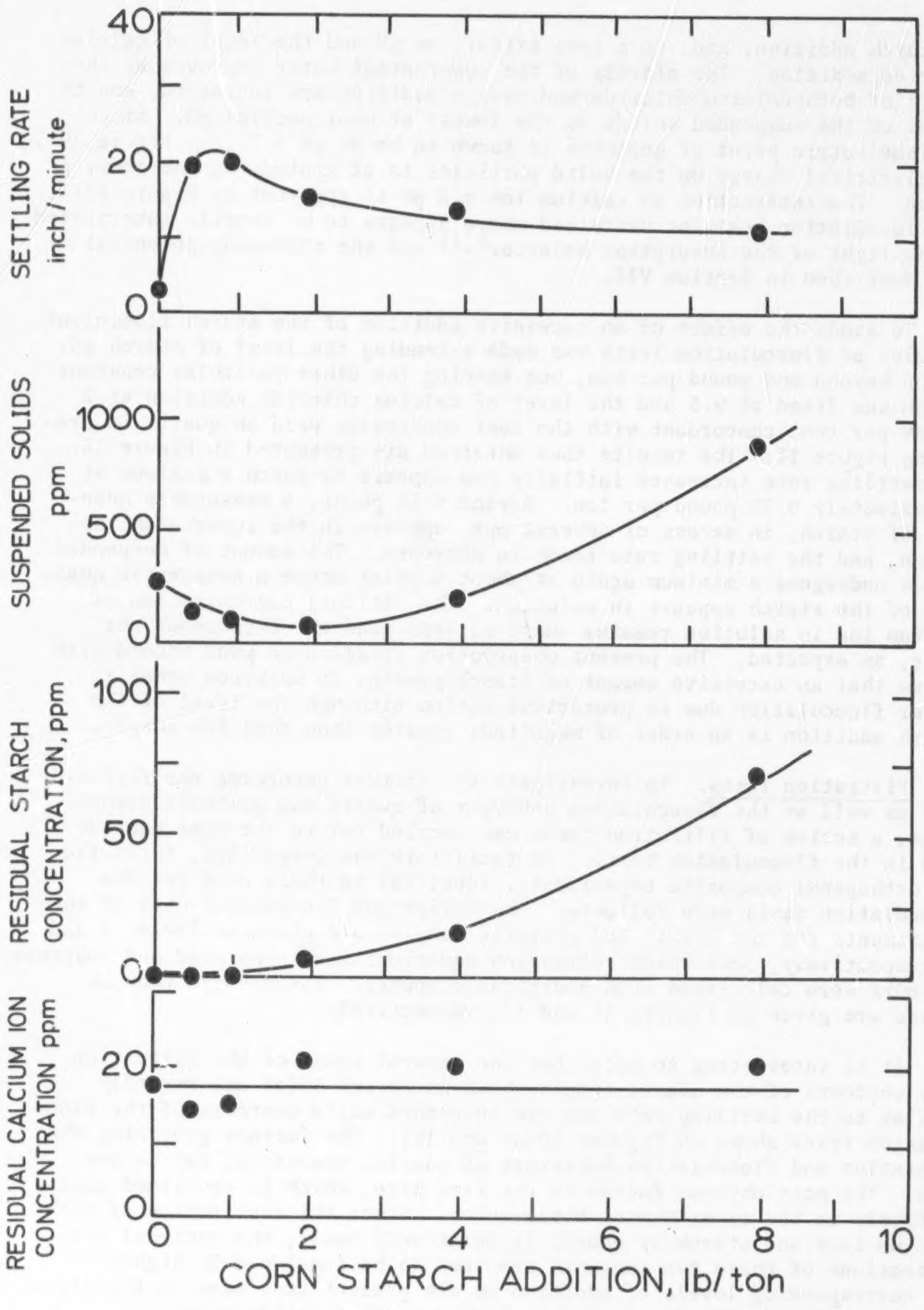
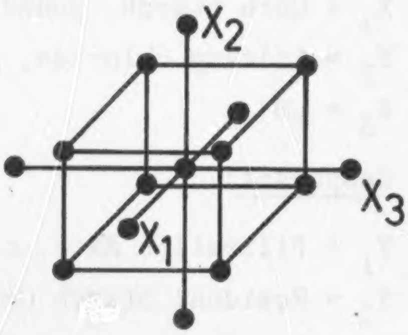


FIGURE 15. Flocculation Test Results on Goethite as Functions of Starch Addition at pH 9.5 and Calcium Chloride Addition of 2 lb per ton

TABLE 4. COMPOSITE DESIGN AND PRODUCT DATA FOR FILTRATION TESTS ON QUARTZ

Factors:

X_1 = Corn Starch, pound per ton
X_2 = Calcium Chloride, pound per ton
X_3 = pH



Responses:

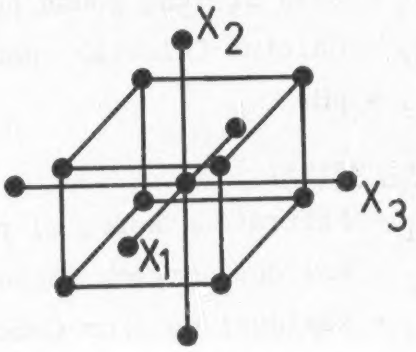
Y_1 = Filtration Rate, ml per minute
Y_2 = Residual Starch Concentration, ppm
Y_3 = Residual Calcium Concentration, ppm

Design Levels			Factor Levels			Responses		
X_1	X_2	X_3	X_1	X_2	X_3	Y_1	Y_2	Y_3
-1	-1	-1	0.09	0.35	7.45	273	1.5	15
1	-1	-1	0.91	0.35	7.45	1.8	38.5	15
-1	1	-1	0.09	3.65	7.45	300	1.5	170
1	1	-1	0.91	3.65	7.45	145	55	175
-1	-1	1	0.09	0.35	11.55	32	0.5	1
1	-1	1	0.91	0.35	11.55	0.6	26.5	1
-1	1	1	0.09	3.65	11.55	343	0.5	142
1	1	1	0.91	3.65	11.55	316	22	142
-1.215	0	0	0.0	2.0	9.5	273	0	92
1.215	0	0	1.0	2.0	9.5	94	59	91
0	-1.215	0	0.5	0.0	9.5	0.9	13	0
0	1.215	0	0.5	4.0	9.5	205	22	185
0	0	-1.215	0.5	2.0	7.0	245	25	92
0	0	1.215	0.5	2.0	12.0	400	0.5	55
0	0	0	0.5	2.0	9.5	226	24	90
1	-1	-1	0.91	0.35	7.45	1.8	39	14
-1	1	-1	0.09	3.65	7.45	300	1.5	171
-1	-1	1	0.09	0.35	11.55	35	0.5	1
1	1	1	0.91	3.65	11.55	333	28	148
0	0	0	0.5	2.0	9.5	218	22	90

TABLE 5. COMPOSITE DESIGN AND PRODUCT DATA FOR FILTRATION TESTS ON GOETHITE

Factors:

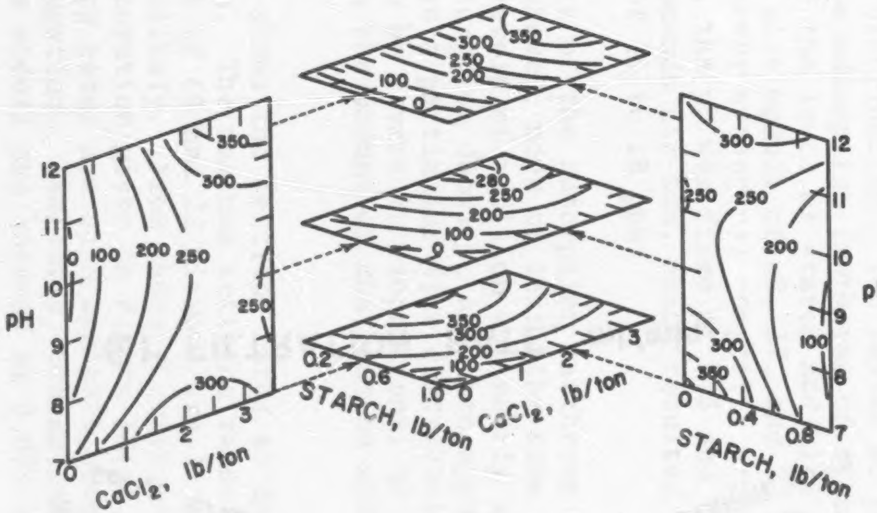
X_1 = Corn Starch, pound per ton
X_2 = Calcium Chloride, pound per ton
X_3 = pH



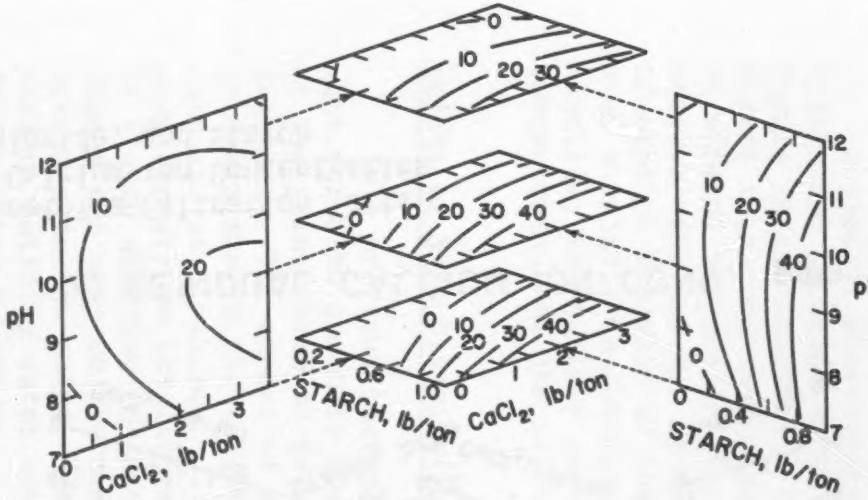
Responses:

Y_1 = Filtration Rate, ml per minute
Y_2 = Residual Starch Concentration, ppm
Y_3 = Residual Calcium Concentration, ppm

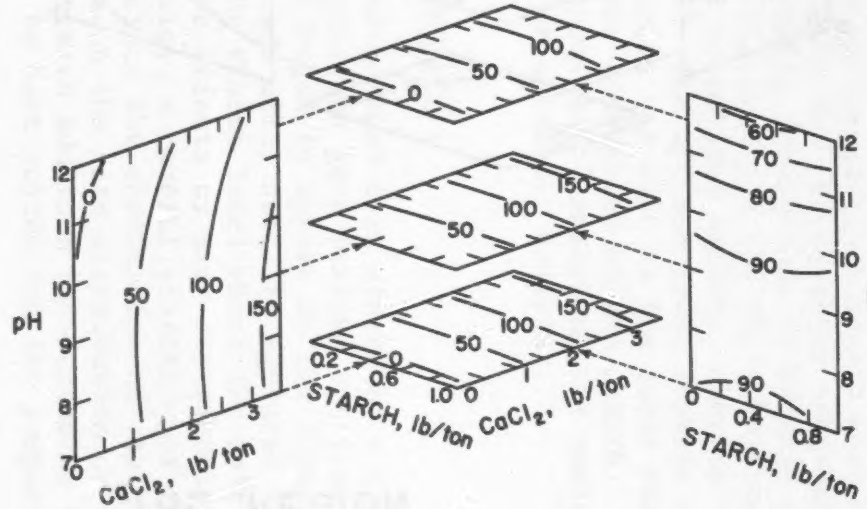
Design Levels			Factor Levels			Responses		
X_1	X_2	X_3	X_1	X_2	X_3	Y_1	Y_2	Y_3
-1	-1	-1	0.09	0.35	7.45	106	1	38
1	-1	-1	0.91	0.35	7.45	214	1	38
-1	1	-1	0.09	3.65	7.45	112	1	201
1	1	-1	0.91	3.65	7.45	197	1	195
-1	-1	1	0.09	0.35	11.55	1.3	1	1
1	-1	1	0.91	0.35	11.55	273	1.5	1
-1	1	1	0.09	3.65	11.55	128	0.5	43
1	1	1	0.91	3.65	11.55	214	0.5	47
-1.215	0	0	0.0	2.0	9.5	102	0	87
1.215	0	0	1.0	2.0	9.5	209	1	87
0	-1.215	0	0.5	0.0	9.5	10	1	0
0	1.215	0	0.5	4.0	9.5	182	1	185
0	0	-1.215	0.5	2.0	7.0	177	1.5	129
0	0	1.215	0.5	2.0	12.0	177	1	0.5
0	0	0	0.5	2.0	9.5	188	0.5	80
1	-1	-1	0.91	0.35	7.45	226	1	37
-1	1	-1	0.09	3.65	7.45	119	0	117
-1	-1	1	0.09	0.35	11.55	1.7	1.5	1
1	1	1	0.91	3.65	11.55	214	0	47
0	0	0	0.5	2.0	9.5	185	1	80



(a) FILTRATION RATE, ml/min.

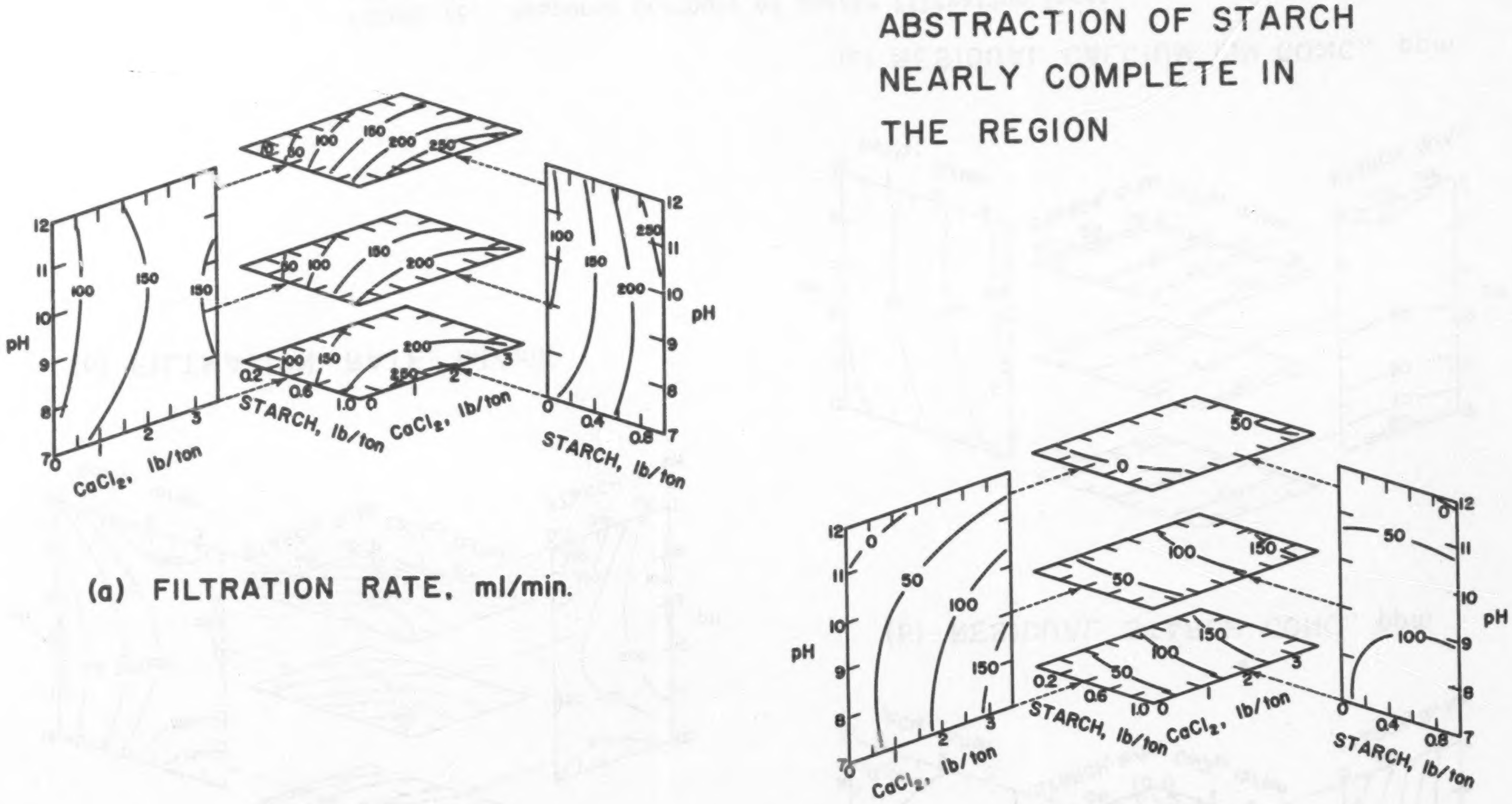


(b) RESIDUAL STARCH CONC., ppm



(c) RESIDUAL CALCIUM ION CONC., ppm

FIGURE 16. Response Contours of Quartz Filtration Tests Filtration Rate (a), Residual Starch Concentration (b), and Residual Calcium-ion Concentration (c) as Functions of pH, Calcium Chloride and Starch



ABSTRACTION OF STARCH NEARLY COMPLETE IN THE REGION

(a) FILTRATION RATE, ml/min.

(c) RESIDUAL CALCIUM ION CONC., ppm

FIGURE 17. Response Contours of Goethite Filtration Tests Filtration Rate (a), and Residual Calcium-ion Concentration (c) as Functions of pH, Calcium Chloride, and Starch

A similar observation may be made on the goethite sample when the filtration behavior shown in Figure 17 and the flocculation behavior in Figure 14 are compared. From the foregoing discussions it becomes apparent that corn starch aids both the flocculation and the clarification of mineral suspensions when it is used in optimum amounts, whereas an excessive addition has an adverse effect. The optimum level depends on the adsorption behavior of the mineral species and also on the total surface area available in the suspension for the adsorption of the starch. In practice, the optimum level may be determined by analyzing the residual concentration of the starch, say with an automatic analyzer.

Effect of Size Distribution and Pulp Density

In a previous section it was reported that corn starch as a flocculant for both goethite and quartz suspensions gave maximum settling rates at the point where an excess of starch began to appear in the supernatant solution. The amount of suspended solids after settling appeared to undergo a mimimum in the neighborhood of the starch level where the settling rate was at a maximum. In studying the effects of size distribution and pulp density on the flocculation behavior, a careful selection of the levels of starch addition becomes important since the abstraction of starch would depend not only on the amount but also on the size distribution of the minerals in the pulp. The levels of starch addition corresponding to the maximum settling rates would probably be best suited for the comparison of flocculation behavior.

In order to establish the levels of starch addition for samples with different size distributions, two series of preliminary tests were performed: (1) the adsorption isotherms of starch and (2) the settling rates as functions of the level of starch addition both on goethite and quartz samples having size moduli of 60, 37, and 22 microns. From the results of the three-factor orthogonal composite experiment reported in Figures 10, 13, and 14, the pH was fixed at 9.5 and the level of calcium chloride addition at 2 pounds per ton, which resulted in a residual calcium-ion concentration of 15 to 18 ppm.

The results of the adsorption isotherms are shown in Figure 18. All the isotherms showed, more or less, the same trend. The abstraction of a starch at low levels of addition was nearly complete, resulting in a steep rise in the adsorption density, and then approached saturation coverage corresponding to a particular size distribution. Since the size modulus may be shown to be inversely proportional to the specific surface area, the increase in the amount of abstraction with smaller size moduli is to be expected.

Figure 19 shows the settling rates as functions of the level of starch addition. The maximum settling rates for the goethite samples of the size moduli of 60 and 22 microns are located at 0.75 and 1.5 pounds per ton, respectively. From these figures and the amounts of starch abstracted at saturation given in Figure 18(a), it is estimated that the maximum settling rates are at a constant coverage of approximately 15 percent of saturation. Similarly, the maximum settling rates for quartz having the same moduli are located at 0.075 and 0.11 pounds per ton, re-

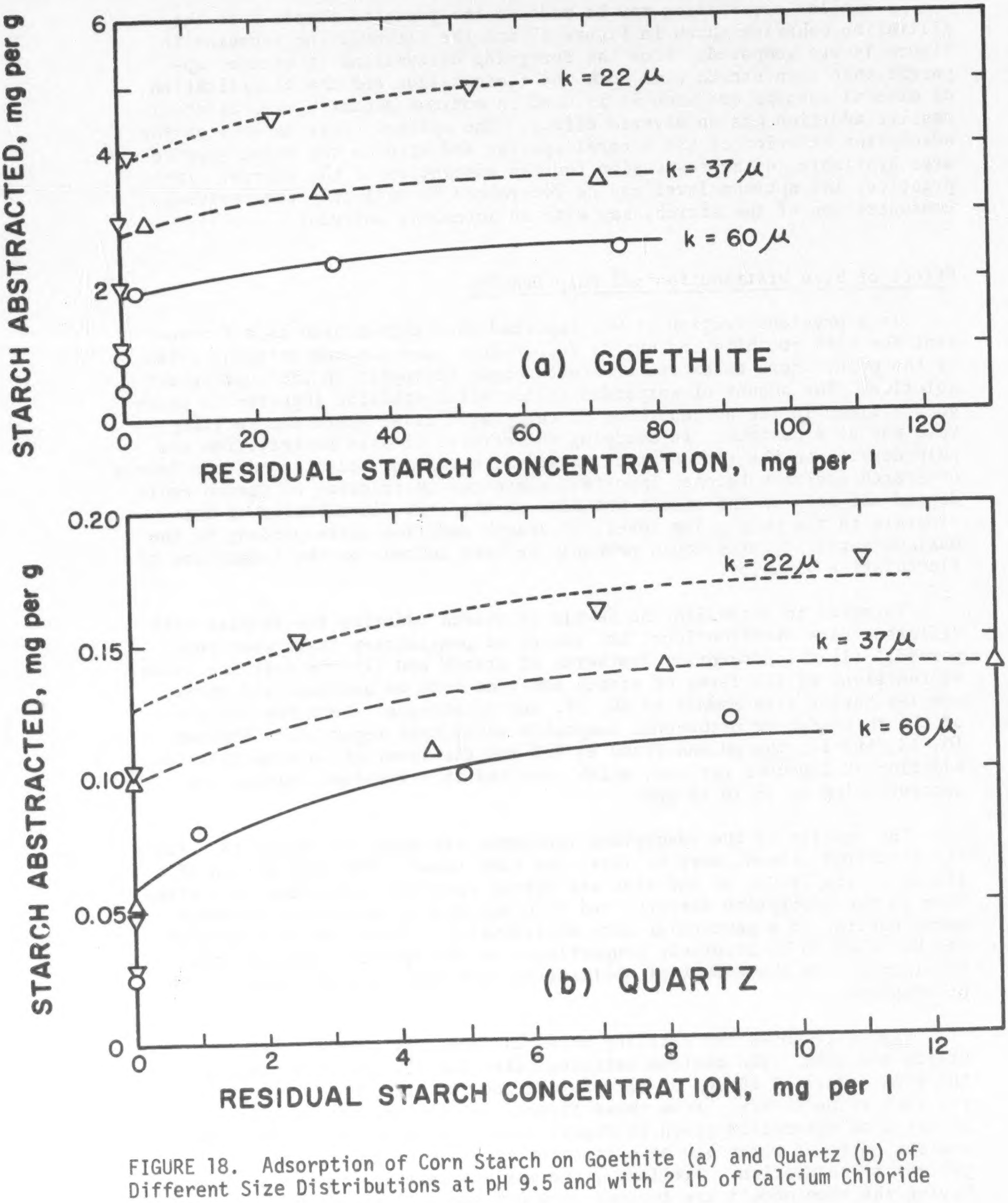


FIGURE 18. Adsorption of Corn Starch on Goethite (a) and Quartz (b) of Different Size Distributions at pH 9.5 and with 2 lb of Calcium Chloride per ton

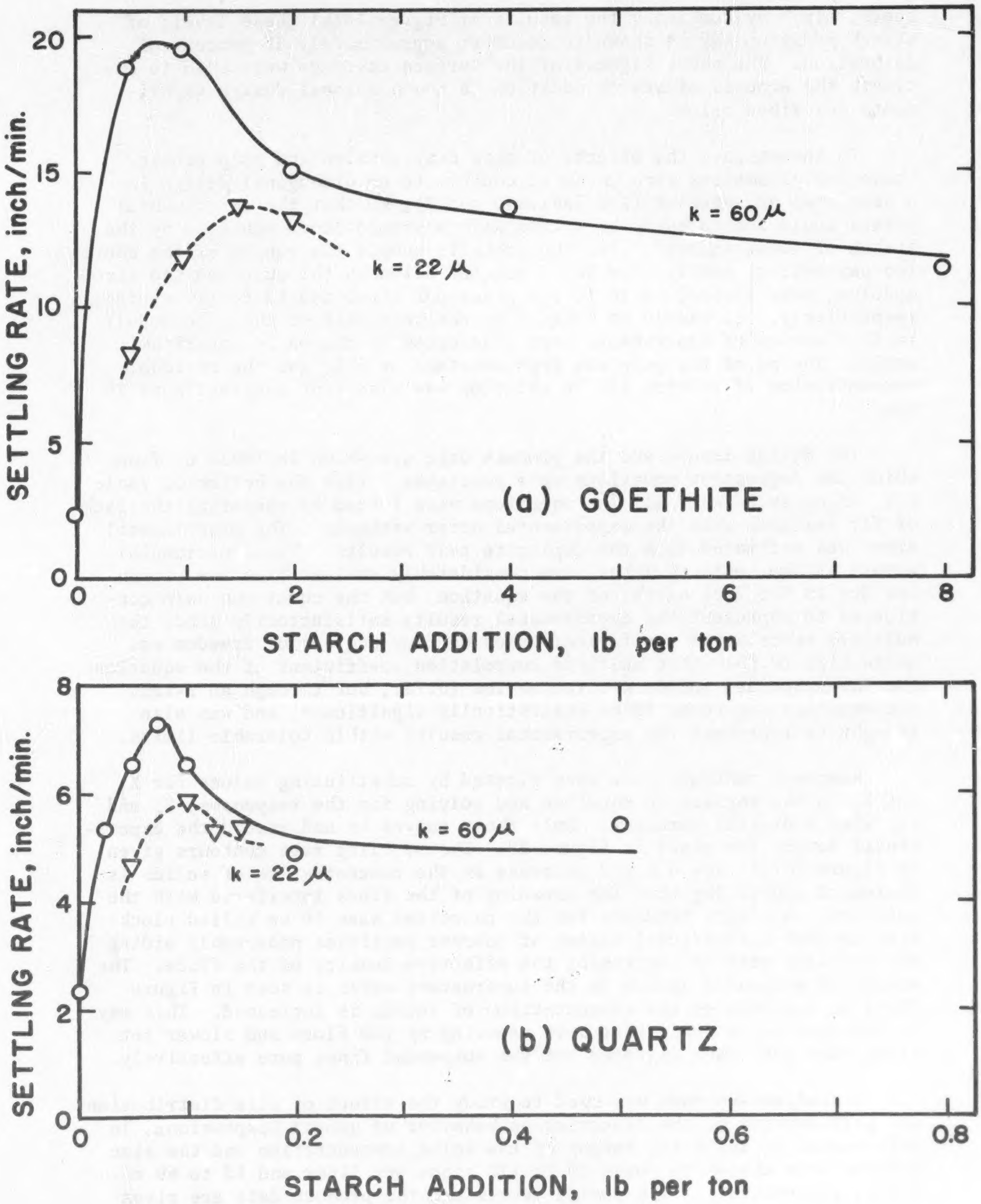


FIGURE 19. Settling Rates of Goethite (a) and Quartz (b) of Different Size Distributions as a Function of Amount of Starch Addition

spectively. By combining the results of Figure 18(b) these levels of starch addition may be shown to occur at approximately 33 percent of saturation. The above figures of the surface coverage were used to estimate the amounts of starch addition in the hexagonal design experiments described below.

To investigate the effects of size distribution and pulp density these two parameters were chosen to conform to an orthogonal design in a hexagonal arrangement (see Tables 6 and 7), so that the experimental points could subsequently be fitted with a second-order equation by the method of least squares. For the goethite sample the ranges of the above two parameters, namely, the solid concentration in the pulp and the size modulus, were limited to 10 to 170 grams per liter and 11 to 110 microns, respectively. It should be noted that the intervals of the size moduli in this series of experiments were inadvertently chosen in logarithmic scale. The pH of the pulp was kept constant at 9.5, and the residual concentration of calcium ion in solution was also kept constant near 16 ppm.

The design levels and the product data are shown in Table 6, from which the regression equations were generated. (See the bottom of Table 6.) Using an F-test, all the equations were tested by comparing the lack of fit variance with the experimental error variance. The experimental error was estimated from the duplicate test results. The experimental errors of the settling rates were considerably smaller than the variances due to the lack of fit of the equation, but the equations were considered to represent the experimental results satisfactorily since the multiple correlation coefficient based on four degrees of freedom was quite high (0.99). The multiple correlation coefficient of the equation for the suspended solids was rather low (0.72), but through an F-test the equation was found to be statistically significant, and was also thought to represent the experimental results within tolerable limits.

Response contours were then plotted by substituting values for X_1 and X_2 in the regression equation and solving for the responses, Y_1 and Y_2, with a digital computer. Only those curves in and around the experimental domain are shown in Figure 20. The settling rate contours given in Figure 20(a) show a rapid decrease as the concentration of solids is increased indicating that the crowding of the flocs interfered with the settling. A slight tendency for the canonical axes to be tilted clockwise implies a beneficial effect of coarser particles presumably aiding the settling rate by increasing the effective density of the flocs. The amount of suspended solids in the supernatant water is seen in Figure 20(b) to decrease as the concentration of solids is increased. This may be interpreted to imply that more crowding by the flocs and slower settling rate must have filtered out the suspended fines more effectively.

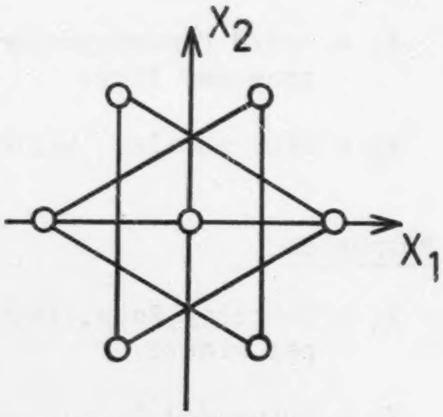
A similar approach was used to study the effect of size distribution and pulp density on the flocculation behavior of quartz suspensions. In this series of tests the ranges of the solid concentration and the size modulus were chosen to cover 10 to 170 grams per liter and 13 to 69 microns, respectively. The design levels and the product data are given in Table 7. The pH of the pulp was again kept constant at 9.5, and the

TABLE 6. HEXAGONAL DESIGN AND PRODUCT DATA FOR FLOCCULATION TESTS ON GOETHITE

Factors:

X_1 = Solid Concentration, gram per liter

X_2 = Logarithm of Size Modulus in Microns



Responses:

Y_1 = Settling Rate, inch per minute

Y_2 = Suspended Solids in Supernate, ppm

Design Levels		Factor Levels		Responses	
X_1	X_2	X_1	X_2*	Y_1	Y_2
1.000	0.0	170	36	3.0	84
0.500	0.866	130	60	6.8	84
-0.500	0.866	50	60	19.6	68
-1.000	0.0	10	36	34.7	636
-0.500	-0.866	50	22	13.7	28
0.500	-0.866	130	22	3.8	84
0	0	90	36	7.8	70
0	0	90	36	8.2	68
1.0	0	170	36	3.7	74
-1.0	0	10	36	32.2	170

*Lists the size moduli of the samples used.

Regression Equations:

$$Y_1 = 28.66 - 0.34X_1 - 6.31X_2 + 0.0016X_1^2 + 7.61X_2^2 - 0.082X_1X_2$$

$$\gamma = 0.99 \quad (\phi = 4)$$

$$Y_2 = -2063 - 4.6X_1 + 3051X_2 + 0.027X_1^2 - 933X_2^2 - 1.1X_1X_2$$

$$\gamma = 0.72 \quad (\phi = 4)$$

TABLE 7. HEXAGONAL DESIGN AND PRODUCT DATA FOR FLOCCULATION TESTS ON QUARTZ

Factors:

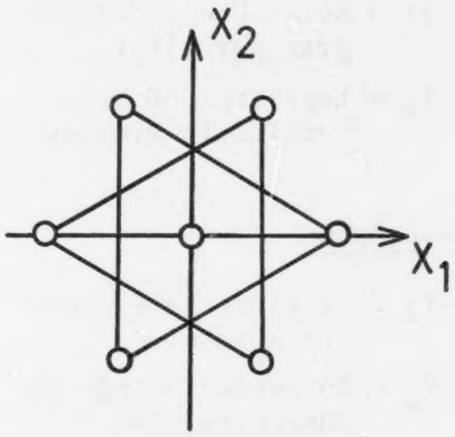
X_1 = Solid Concentration, gram per liter

X_2 = Size modulus, microns

Responses:

Y_1 = Settling Rate, inch per minute

Y_2 = Suspended Solids in Supernate, ppm



Design Levels		Factor Levels		Responses	
X_1	X_2	X_1	X_2	Y_1	Y_2
1.000	0.0	170	41	2.0	2840
0.500	0.866	130	60	3.4	1520
-0.500	0.866	50	60	7.3	1740
-1.000	0.0	10	41	0.2	350
-0.500	-0.866	50	22	5.2	5290
0.500	-0.866	130	22	2.3	6170
0	0	90	41	4.4	2100
0	0	90	41	4.6	2300
1.0	0	170	41	2.1	2960
-1.0	0	10	41	0.2	340

Regression Equations:

$$Y_1 = 1.383 + 0.109X_1 - 0.131X_2 - 0.00053X_1^2 + 0.0025X_2^2 - 0.00033X_1X_2$$

$$\gamma = 0.96 \quad (\phi = 4)$$

$$Y_2 = 10898 + 45X_1 - 444X_2 - 0.090X_1^2 + 4.5X_2^2 - 0.36X_1X_2$$

$$\gamma = 0.99 \quad (\phi = 4)$$

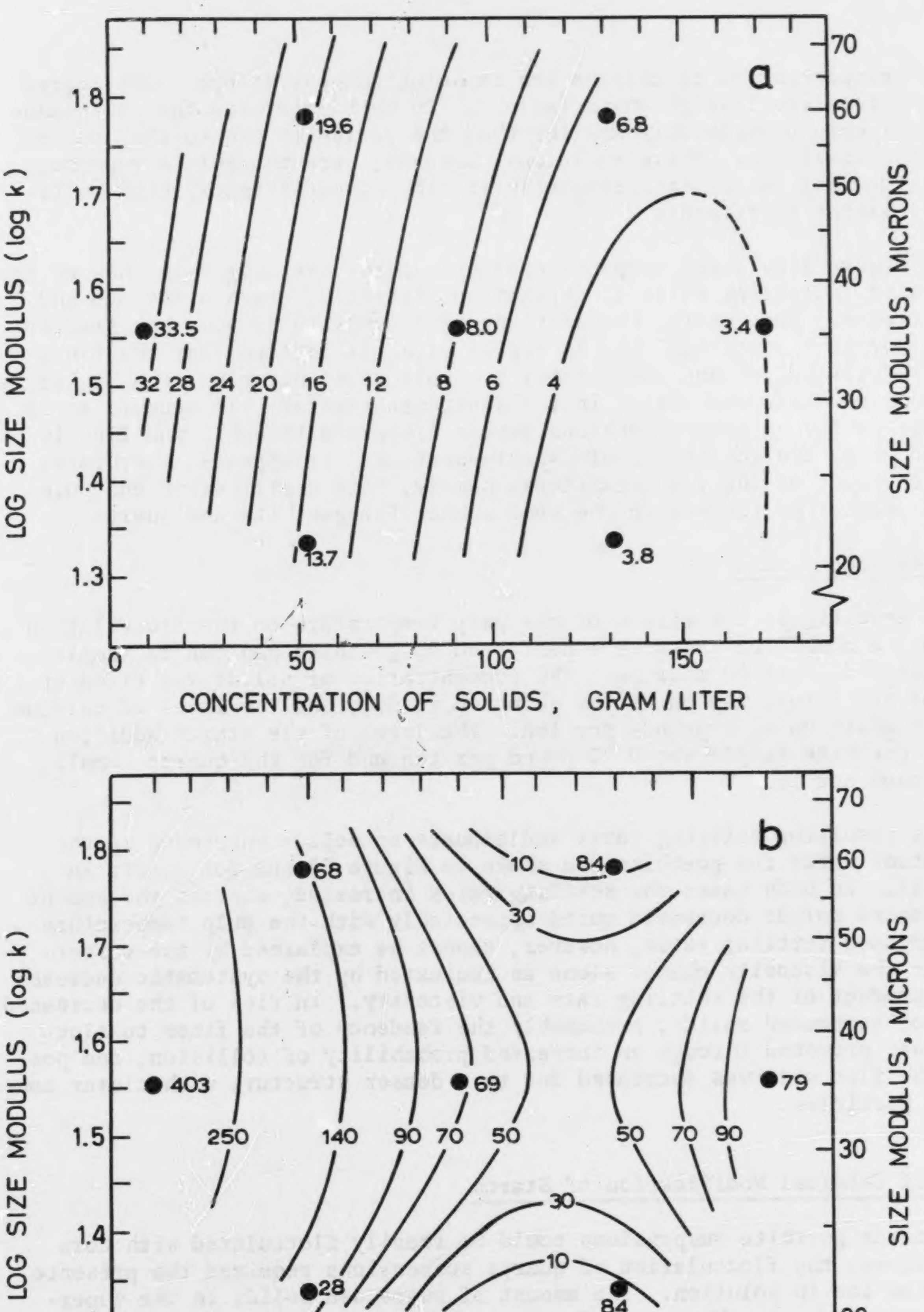


FIGURE 20. Response Contours of Flocculation Test Results on Goethite as Functions of Size Modulus and Concentration of Solids (a) Settling Rate, (b) Suspended Solids Concentration in Supernate

residual concentration of calcium ion in solution near 16 ppm. The regression equations are also given in Table 7. In both equations the experimental errors were considerably smaller than the variances due to the lack of fit of the equations. These equations, however, were thought to represent the experimental points satisfactorily in view of sufficiently high multiple correlation coefficents.

In Figure 21(a), the response contours of the settling rate show an increase with increasing solid concentration initially, reach a maximum and then decrease. Here again, the settling rate tends to be somewhat greater for coarser size distribution. In Figure 21(b) it is seen that the finer the size distribution and the greater the solid concentration, the higher is the amount of suspended solids in the supernatant water. It appears as if the fines in the quartz suspensions remain dispersed though a mud line is observed under the conditions of experimentation. It appears, therefore, that the effect of the two parameters, namely, size distribution and pulp density, cannot be treated in the same manner for goethite and quartz.

Effect of Temperature

To investigate the effect of the pulp temperature on the flocculation behavior, a number of tests were performed on goethite and quartz samples with size moduli of 60 microns. The concentration of solids was fixed at 50 grams per liter, the pH of the solution at 9.5, and the level of calcium chloride addition at 2 pounds per ton. The level of the starch addition for the goethite sample was 0.75 pound per ton and for the quartz sample, 0.075 pound per ton.

The resulting settling rates and amounts of solids suspended in the supernatant water for goethite are shown in Figure 22 and for quartz in Figure 23. In both cases the settling rates increased, whereas the amount of suspended solids decreased quite appreciably with the pulp temperature. The increased settling rates, however, cannot be explained by the correction for the viscosity change alone as indicated by the systematic decrease of the product of the settling rate and viscosity. In view of the decreased amount of suspended solids, presumably the tendency of the fines to flocculate was promoted through an increased probability of collision, and possibly the floc size was decreased due to a denser structure with closer contact of particles.

Effect of Chemical Modification of Starch

Whereas goethite suspensions could be readily flocculated with corn starch alone, the flocculation of quartz suspensions required the presence of calcium ion in solution. The amount of suspended solids in the supernatant liquor was in the range of several hundred ppm even when a fairly large quantity of calcium chloride was added. The calcium ion adsorbed on the quartz surface increased the adsorption of starch and hence the flocculation. It became of interest, therefore, to study the uses of cationic starch, particularly in the flocculation of quartz. The adsorption density

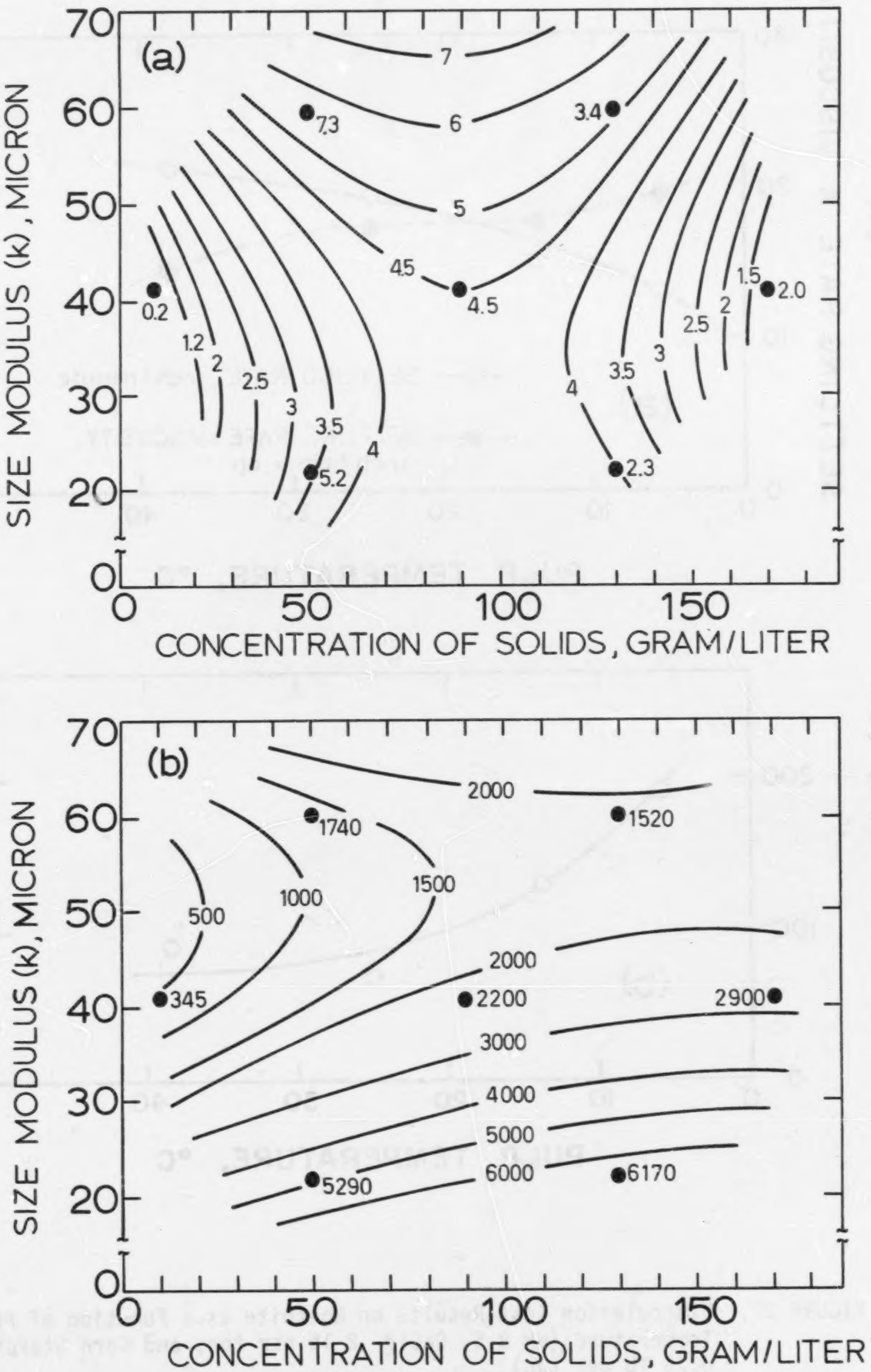


FIGURE 21. Response Contours of Flocculation Test Results on Quartz as Functions of Size Modulus and Concentration of Solids (a) Settling Rate, (b) Suspended Solids Concentration in Supernate

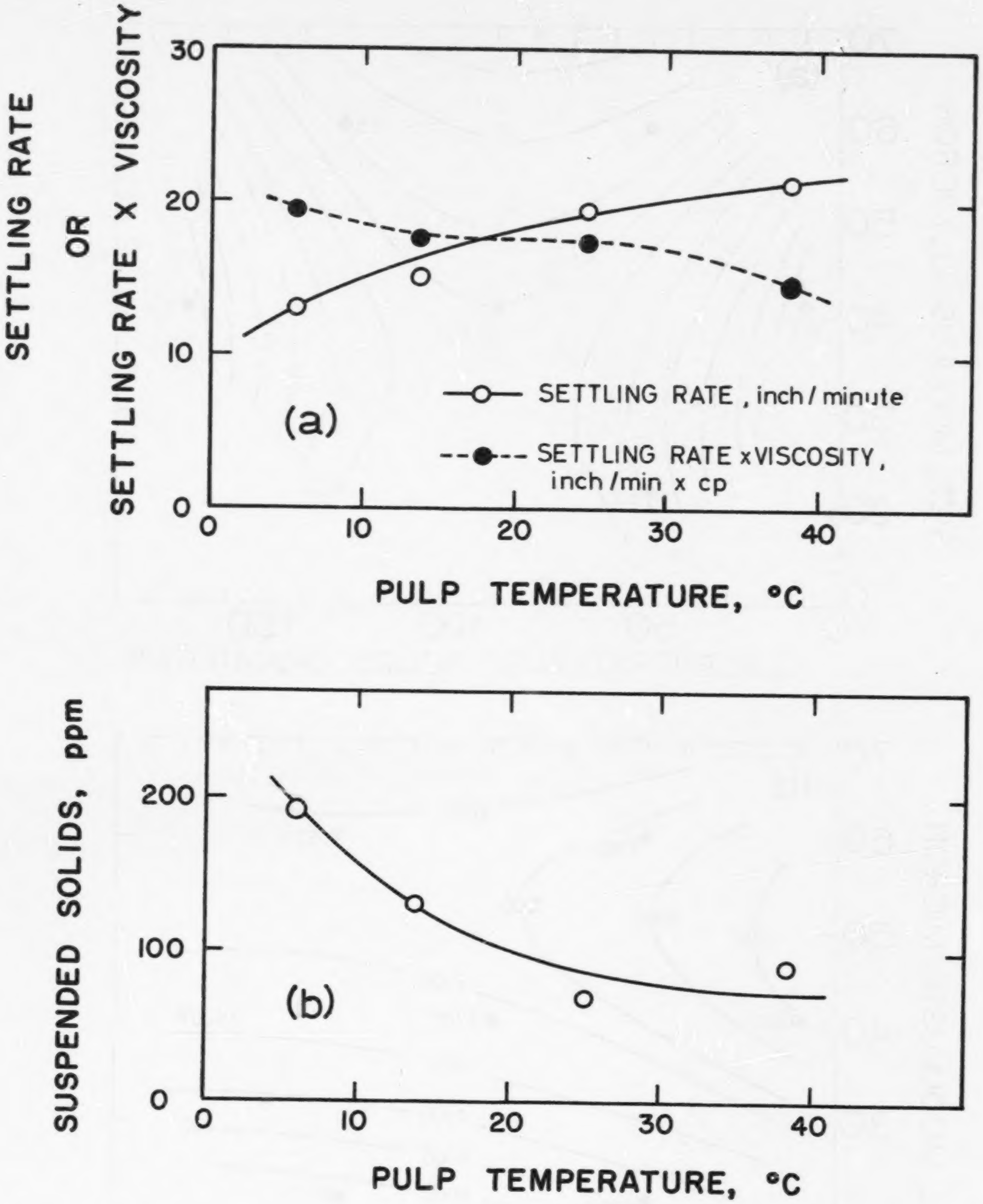


FIGURE 22. Flocculation Test Results on Goethite as a Function of Pulp Temperature (pH 9.5, $CaCl_2$ 2 lb per ton, and Corn Starch 0.75 lb per ton)

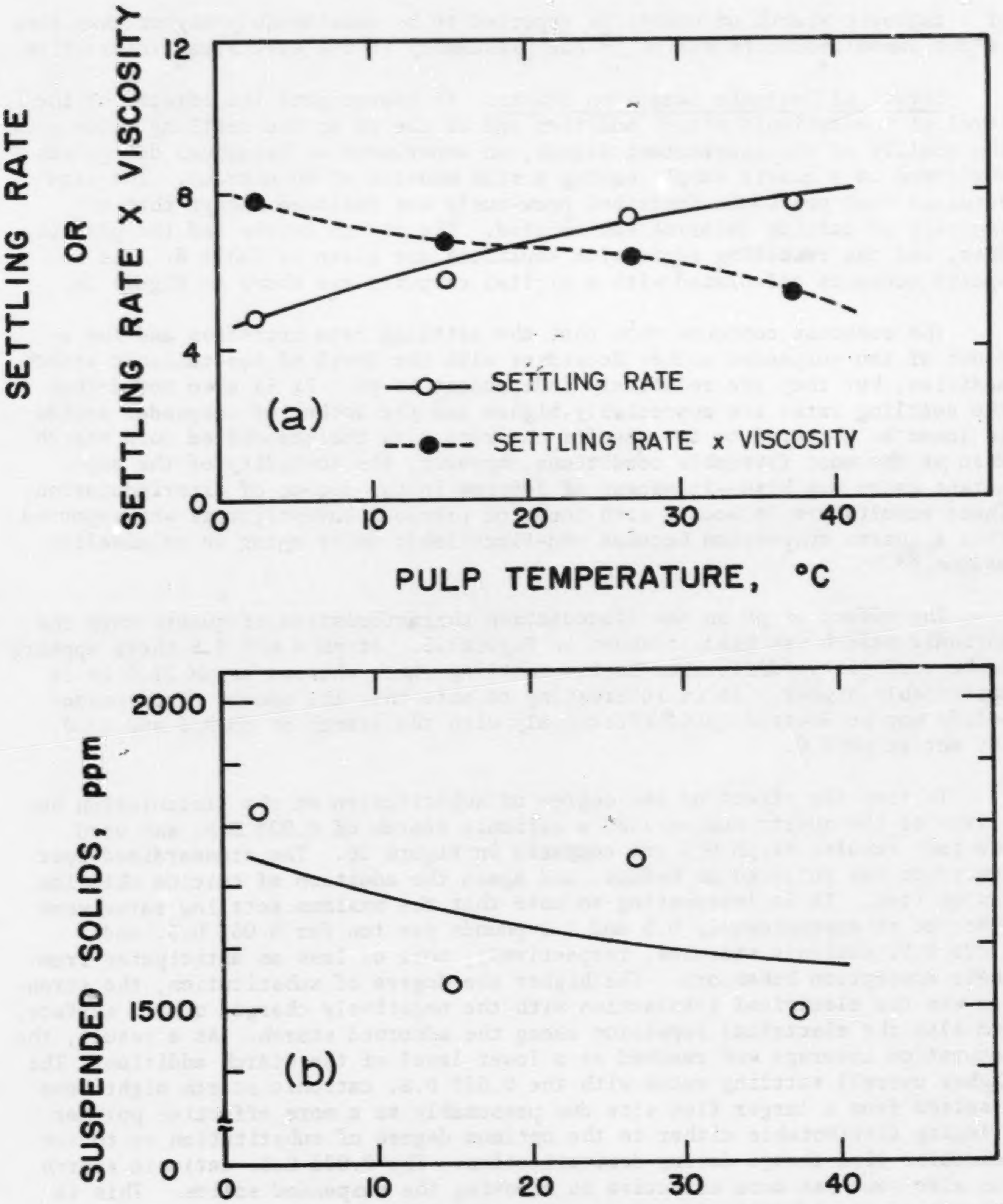


FIGURE 23. Flocculation Test Results on Quartz as a Function of Pulp Temperature (pH 9.5, $CaCl_2$ 2 lb per ton, and Corn Starch 0.075 lb per ton)

of a cationic starch on quartz is reported to be considerably higher than that of the unmodified corn starch,[15] due presumably to the electrical interaction.

Effect of Cationic Starch on Quartz. To investigate the effects of the level of the cationic starch addition and of the pH on the settling rates and the quality of the supernatant liquor, an experiment of hexagonal design was performed on a quartz sample having a size modulus of 60 microns. The standardized test procedure described previously was followed except that the addition of calcium chloride was omitted. The design levels and the product data, and the resulting regression equations are given in Table 8. The response contours calculated with a digital computer are shown in Figure 24.

The response contours show that the settling rate increases and the amount of the suspended solids decreases with the level of the cationic starch addition, but they are relatively independent of pH. It is also noted that the settling rates are appreciably higher and the amount of suspended solids is lower as compared to the results observed with the unmodified corn starch. Even at the most favorable conditions, however, the turbidity of the supernatant water was high--in excess of 100 ppm in the region of experimentation. These results are in accord with those of previous investigators who reported that a quartz suspension becomes non-flocculable after aging in an alkaline medium.[24]

The effect of pH on the flocculation characteristics of quartz when the cationic starch was used is shown in Figure 25. At pH 4 and 9.5 there appears to be very little difference in the settling rate, whereas at pH 11.0 it is appreciably higher. It is interesting to note that the amount of suspended solids may be lowered quite effectively with the starch at pH 9.5 and 11.0, but not at pH 4.0.

To test the effect of the degree of substitution on the flocculation behavior of the quartz suspension, a cationic starch of 0.023 D.S. was used. The test results at pH 9.5 are compared in Figure 26. The standardized test procedure was followed as before, and again the addition of calcium chloride was omitted. It is interesting to note that the maximum settling rates were observed at approximately 0.5 and 1.2 pounds per ton for 0.067 D.S. and 0.023 D.S. cationic starches, respectively, more or less as anticipated from their adsorption behaviors. The higher the degree of substitution, the stronger was the electrical interaction with the negatively charged quartz surface, and also the electrical repulsion among the adsorbed starch. As a result, the saturation coverage was reached at a lower level of the starch addition. The higher overall settling rates with the 0.023 D.S. cationic starch might have resulted from a larger floc size due presumably to a more effective polymer bridging attributable either to the optimum degree of substitution or to the molecular size change during derivatization. The 0.023 D.S. cationic starch was also somewhat more effective in removing the suspended solids. This is a point of considerable importance since the clarification of the quartz suspension is known to be difficult. Further investigation through adsorption measurements and streaming potential measurements using cationic starches of different degrees of substitution becomes of interest.

TABLE 8. HEXAGONAL DESIGN AND PRODUCT DATA FOR FLOCCULATION TESTS ON QUARTZ

Factors:

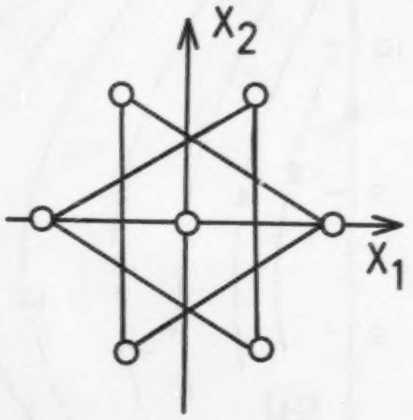
X_1 = 0.067 D.S. Cationic Starch, Pound per ton

X_2 = pH

Responses:

Y_1 = Settling Rate, inch per minute

Y_2 = Suspended Solids in Supernate, ppm



Design Levels		Factor Levels		Responses	
X_1	X_2	X_1	X_2	Y_1	Y_2
1.000	0.0	1.0	9.5	11.2	230
0.500	0.866	0.75	11.0	12.6	450
-0.500	0.866	0.25	11.0	12.6	640
-1.000	0.0	0.0	9.5	0	3080
-0.500	-0.866	0.25	8.0	8.4	220
0.500	-0.866	0.75	8.0	10.6	160
0	0	0.5	9.5	11.6	210
0	0	0.5	9.5	10.6	180
1.0	0	1.0	9.5	10.4	270
-1.0	0	0.0	9.5	0	2940

Regression Equations:

$$Y_1 = 39.23 + 45.81X_1 - 9.84X_2 - 22.80X_1^2 + 0.61X_2^2 - 1.47X_1X_2$$

$$\gamma = 0.96 \qquad (\phi = 4)$$

$$Y_2 = -6248 - 7175X_1 + 1734X_2 + 5740X_1^2 - 83X_2^2 - 87X_1X_2$$

$$\gamma = 0.95 \qquad (\phi = 4)$$

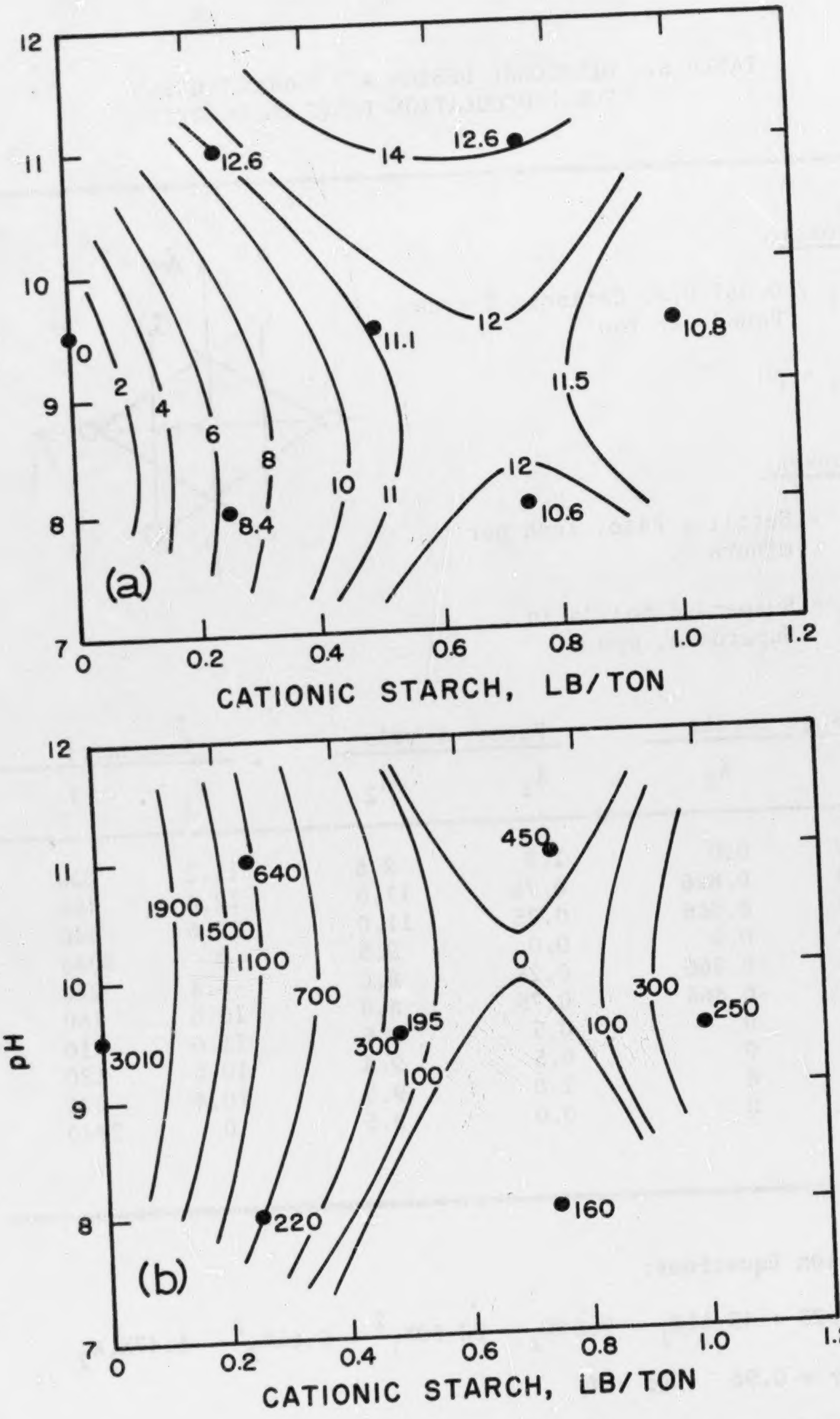


FIGURE 24. Response Contours of Flocculation Test Results on Quartz as a Function of Amount of Cationic Starch (0.067 D.S.) and of pH

(a) Settling Rate, (b) Suspended Solids Concentration in Supernate

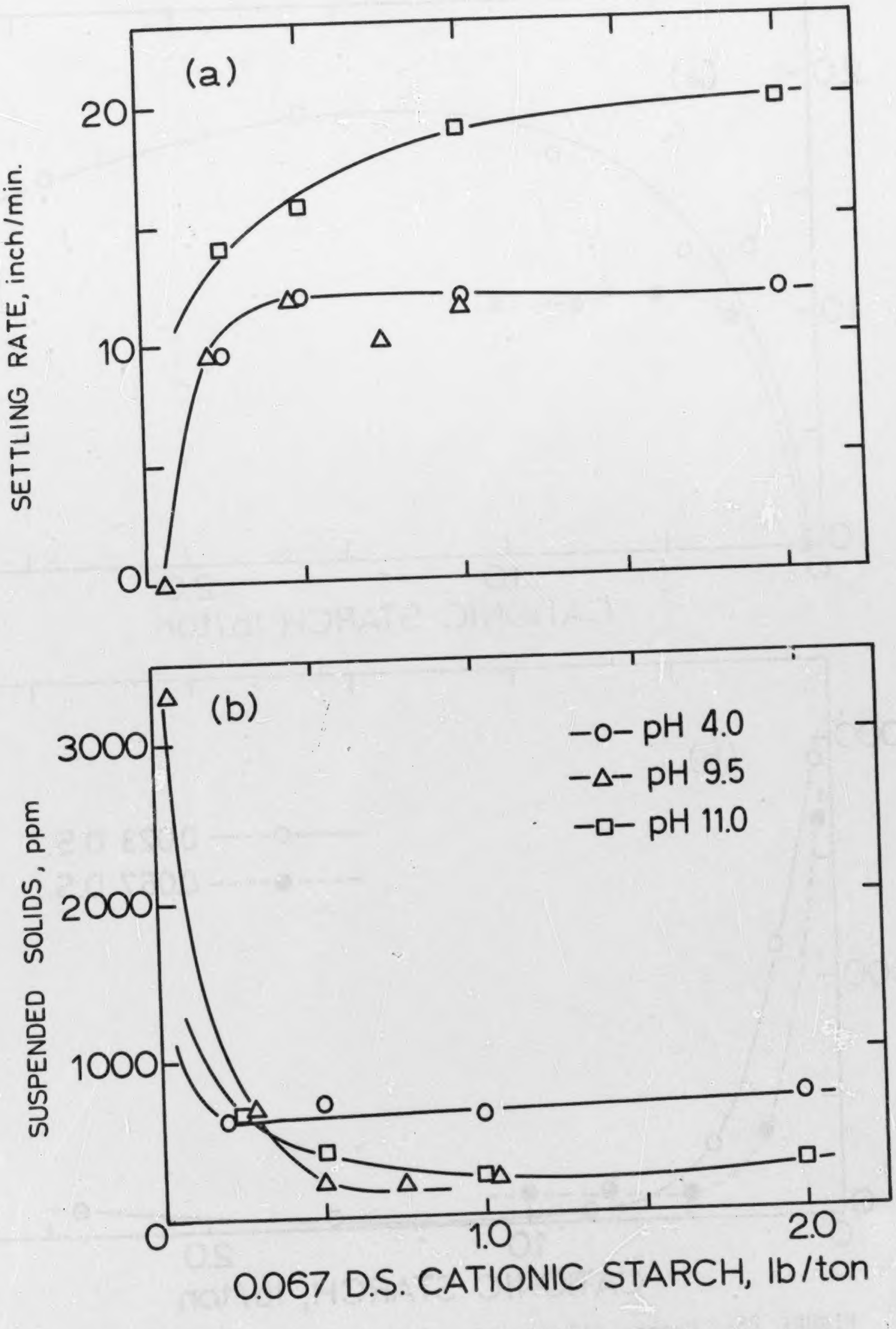


FIGURE 25. The Effect of pH on the Flocculation Test Results on Quartz as a Function of 0.067 D.S. Cationic Starch Addition

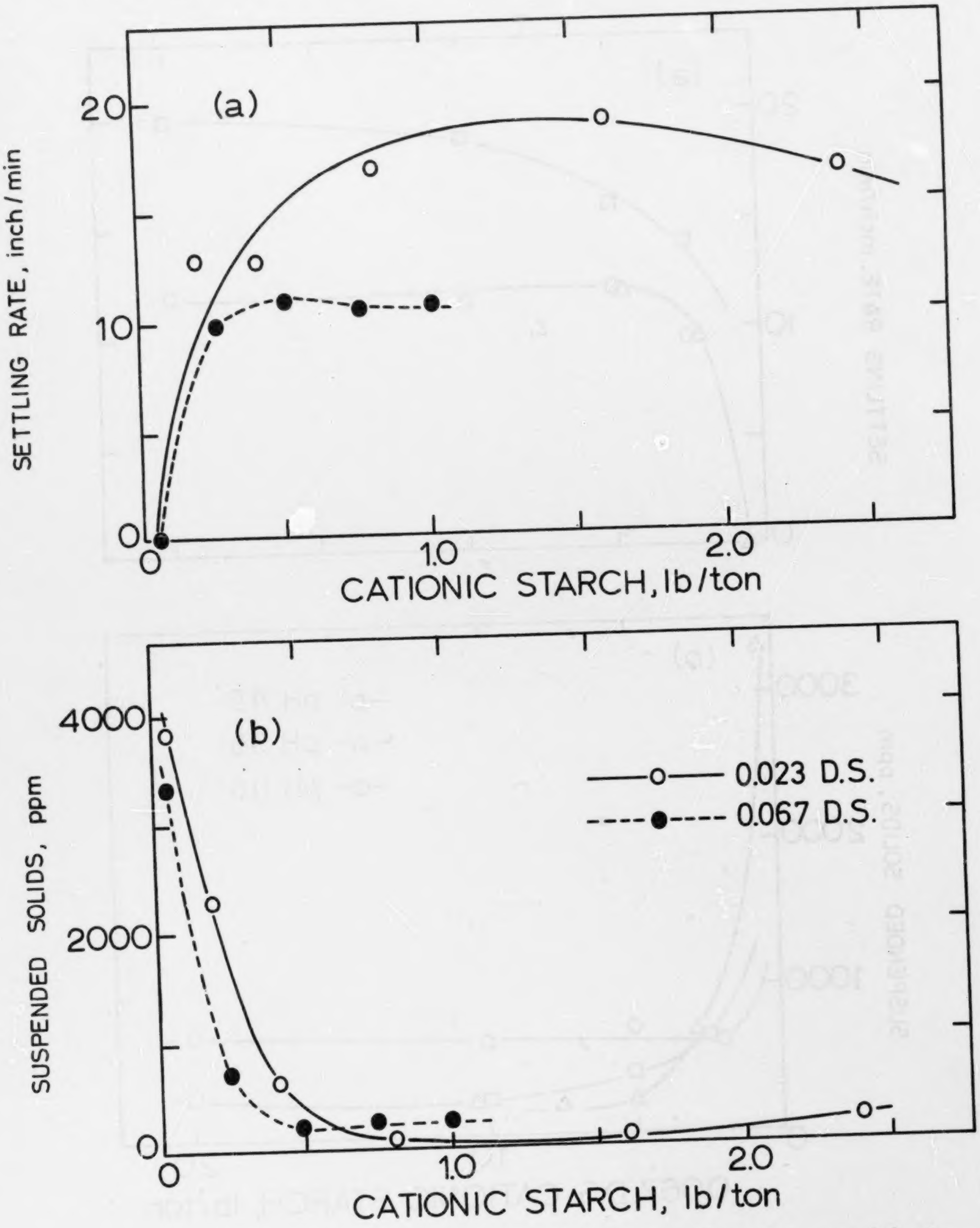


FIGURE 26. Graphs Illustrating (a) the Settling Rate and (b) the Amount of Suspended Solids in Supernatant Water of Quartz as Functions of the Levels of Two Different Cationic Starches at pH 9.5

Effect of Cationic Starch on Goethite. The flocculation behavior of a goethite suspension with the 0.067 D.S. cationic starch was investigated briefly. The experimental procedure was the same as that used previously: 50 grams of a goethite sample per liter at pH 9.5 and no addition of calcium chloride. The results are shown in Figure 27. As expected, the cationic starch was as effective as the unmodified corn starch in flocculating and clarifying the goethite suspension. No further attempt was made, therefore, to elaborate the flocculation behavior of goethite suspensions with cationic starches.

Effect of Anionic Starch on Quartz. Quartz suspensions cannot be flocculated with either an unmodified corn starch or an anionic starch alone. Only when these reagents are used in combination with calcium ions can quartz suspensions be flocculated. To investigate the effect of the level of addition of 0.93 D.S. carboxymethyl starch, a number of tests were performed on a quartz suspension of 50 grams per liter at pH 9.5. The standardized test procedure including the initial conditioning with 2 pounds of calcium chloride per ton was followed. The results are given in Figure 28. It is noted that the maximum settling rate was observed at 0.04 pound per ton, which is approximately one-half of the level of unmodified corn starch addition of 0.075 pound per ton. (See Figure 11.) The amount of suspended solids remained in excess of 1000 ppm in the presence of the starch.

The effect of the level of calcium chloride addition was investigated next by fixing the starch level at 0.05 pound per ton. The results thus obtained are shown in Figure 29. The maximum settling rate and the minimum level of the suspended solids were observed at 3 pounds of calcium chloride per ton, beyond which both the settling rate and the amount of suspended solids remained more or less constant. It appears, therefore, that the clarity of the supernatant water may not be improved beyond 1000 ppm when an anionic starch is used as a polymeric flocculant.

Effect of Anionic Starch on Goethite. Goethite suspensions at pH 9.5 could not be flocculated with the 0.93 D.S. carboxymethyl starch at 0.1 or 0.5 pound per ton in the absence of calcium chloride. This was, more or less, as expected since both the goethite surface and the starch are negatively charged.

Effect of Dodecylammonium or Aluminum Ion

In a previous section it was mentioned that a quartz surface might become hydrophilic in water, and that a quartz suspension might become nonflocculable. It is well known in ore flotation that a quartz surface may be made hydrophobic with a long-chain aklylammonium salt, thereby rendering the quartz particle floatable upon introduction of air bubbles. At this point the sign of the zeta potential on quartz is reversed.[26] These two points, namely, the hydrophobic surface and the reversal of the sign of the zeta potential, become of particular interest in inducing the flocculation condition for quartz suspensions.

A few preliminary tests were performed by conditioning a quartz suspension

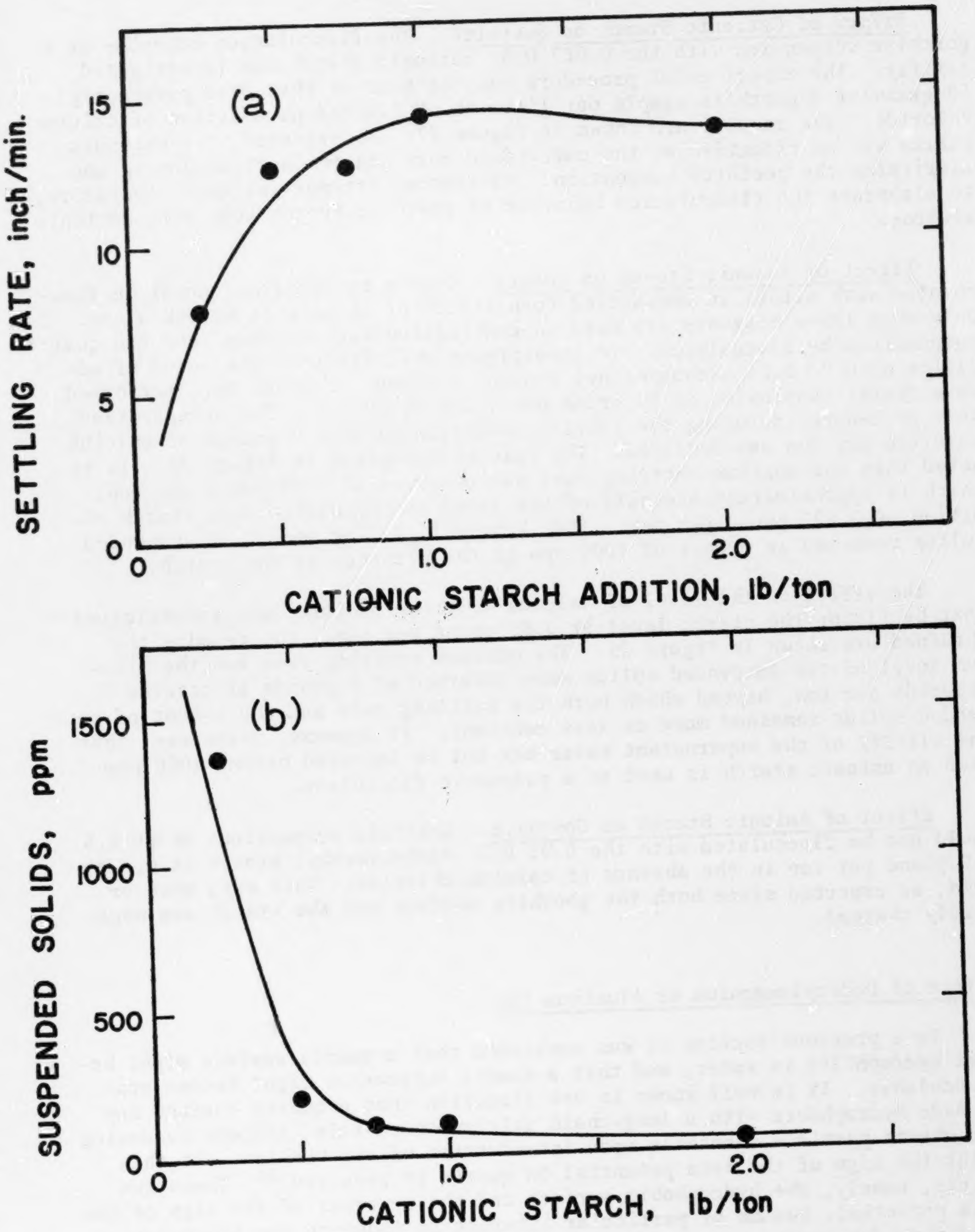


FIGURE 27. Flocculation Test Results on Goethite as a Function of 0.067 D.S. Cationic Starch Addition at pH 9.5

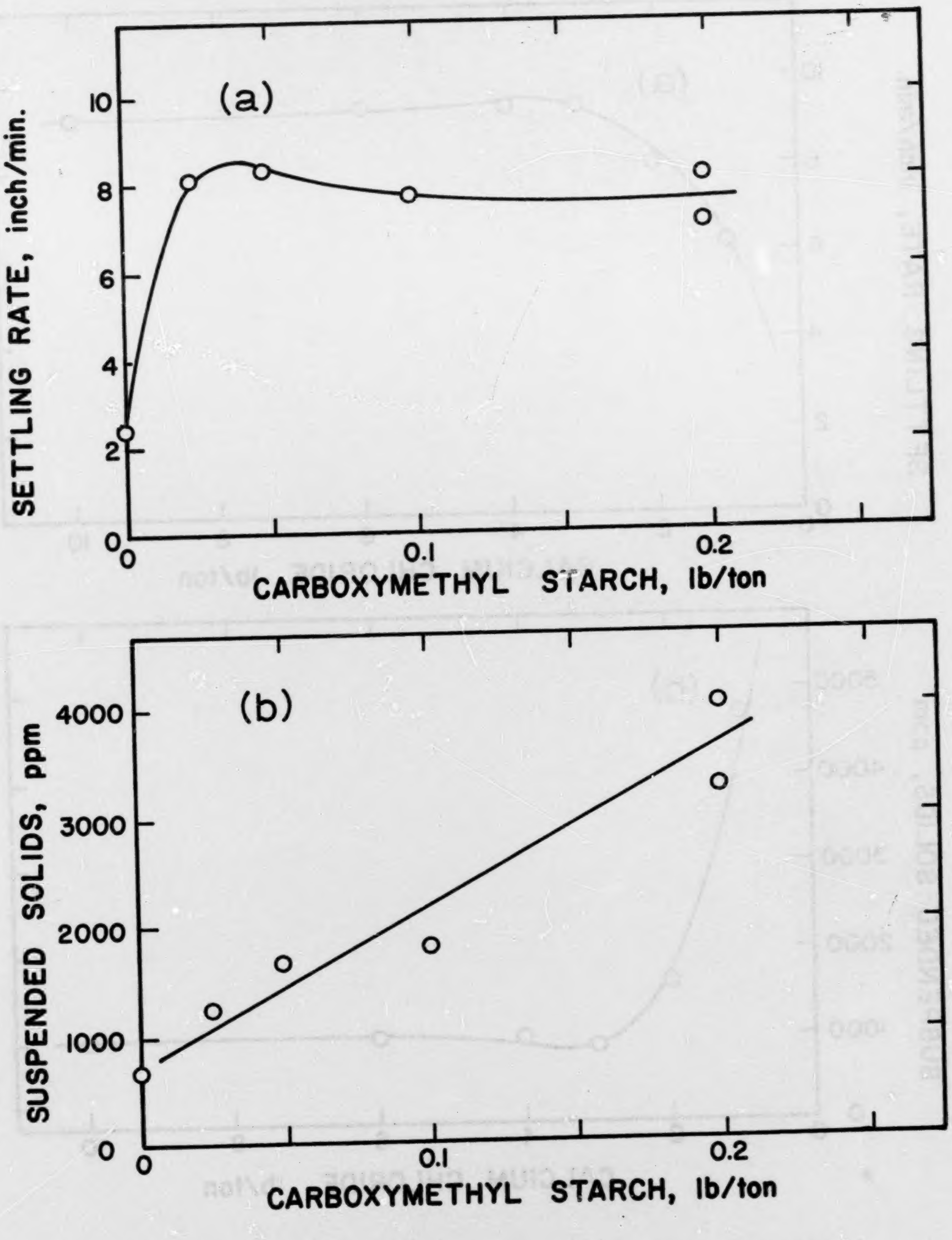


FIGURE 28. Flocculation Test Results on Quartz as a Function of 0.93 D.S. Carboxymethyl Starch Addition at pH 9.5; Calcium Chloride 2 lb per ton

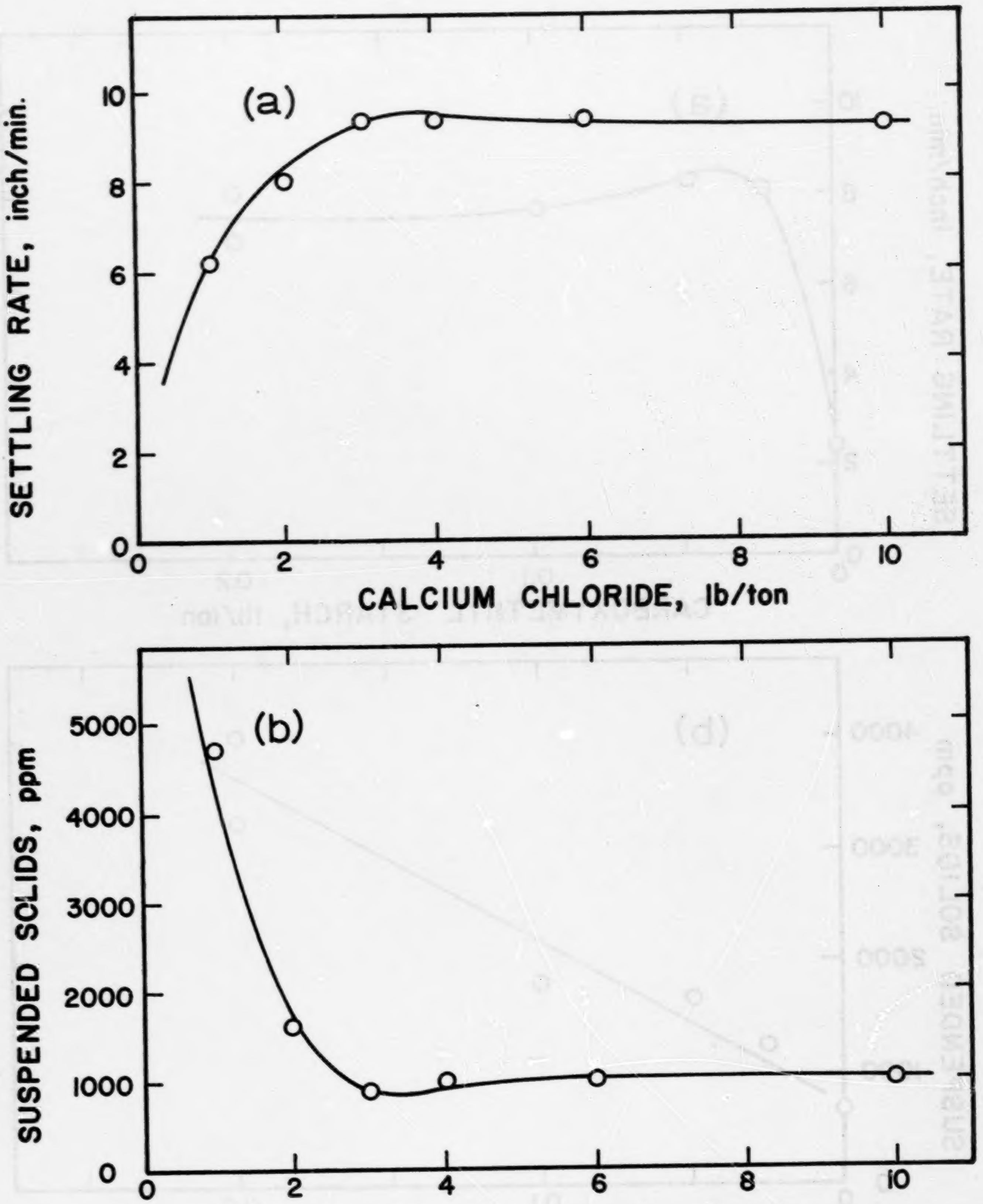


FIGURE 29. Flocculation Test Results on Quartz as a Function of Calcium Chloride Addition at pH 9.5; 0.93 D.S. Carboxymethyl Starch 0.05 lb per ton

initially with different amounts of dodecylammonium chloride instead of with calcium chloride, and then adding 0.075 pound of unmodified corn starch per ton. The pH of the suspension was kept at pH 9.5. The results of the flocculation tests are shown in Figure 30. In the bottom of the figure the residual concentrations of dodecylamine in the supernatant solution, which were determined colorimetrically, are included.

If these results are compared with the results presented in Figure 11, it is readily apparent that the amount of suspended solids is markedly less, although further optimization studies are needed to ascertain the minimum attainable. An increase in the amount of corn starch to 0.15 pound per ton resulted in increased turbidity of the supernatant water.

As will be shown in the chapter covering the streaming-potential measurements, calcium ion is not effective in reversing the sign of the zeta potential of quartz at near neutral pH. It is possible only when at relatively high concentrations of calcium chloride and at high pH. Since aluminum nitrate is known to reverse the sign of the zeta potential on quartz at a relatively low concentration (2.5×10^{-6} M),[11] a few cursory tests were performed to investigate the effect of this electrolyte together with corn starch, particularly for the clarification of the supernatant solution. Due to the hydrolysis of aluminum nitrate the flocculation behavior of quartz appeared to be complexly dependent not only on the aluminum ion and starch concentrations, but also on the pH. It becomes of much interest to pursue this line of approach further for developing a method of clarifying quartz suspensions, particularly after an alkaline treatment.

Flocculation Tests Using Synthetic Polymers

To compare the relative efficacies of synthetic polymers with starch products for their flocculation and clarification behaviors on quartz the following four polyacrylamides, viz., Separan NP-10, Separan NP-20, Separan AP-30, and NC 1733 were selected on the basis of their ionic character and their nominal molecular weight.[17] The flocculation and clarification behaviors of a quartz sample with a size modulus of 60 microns were determined in the same manner as for the starch flocculants, and the results in the absence and in the presence of 2 pounds of calcium chloride per ton are presented in Figure 31. The pH of the suspensions was fixed at 9.5 for comparison with the previous data using starch flocculants.

It is noted in the figure that non-ionic Separan NP-10 is the best flocculant for the quartz suspension although anionic AP-30 in conjunction with calcium chloride approaches the results with Separan NP-10 at low levels of their addition. Though the addition of calcium chloride appeared to affect the settling rate very little, the amount of suspended solids in supernatant water, particularly when anionic Separan AP-30 was used together with calcium chloride, was lowered appreciably. Cationic NC 1733 was found to be the least effective of the three synthetic polymers tested. The level of the polymer addition at which the maximum of the settling rate is observed

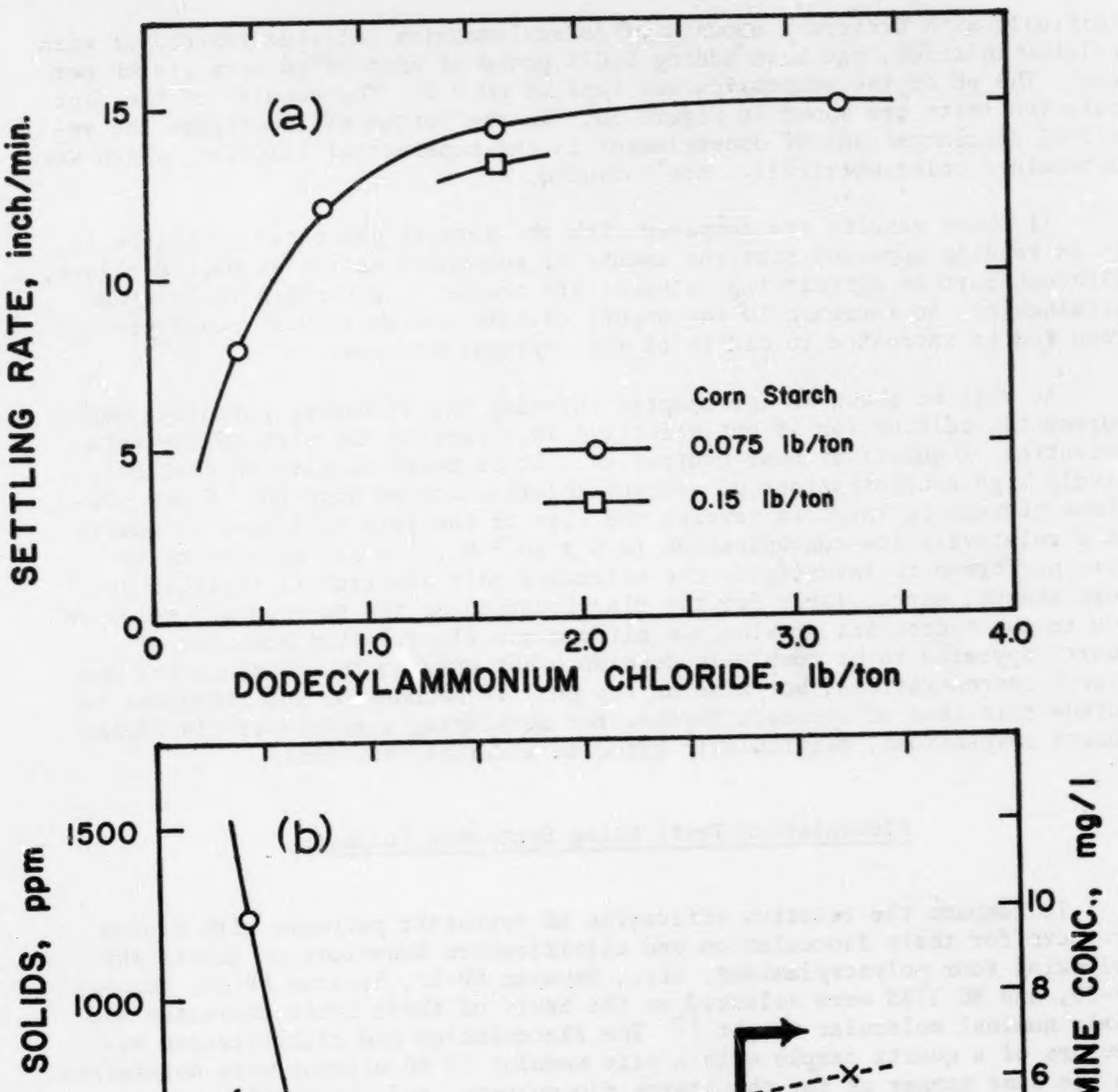


FIGURE 30. Flocculation Test Results on Quartz as a Function of Dodecylammonium Chloride Addition at pH 9.5; Unmodified Corn Starch 0.075 lb per ton

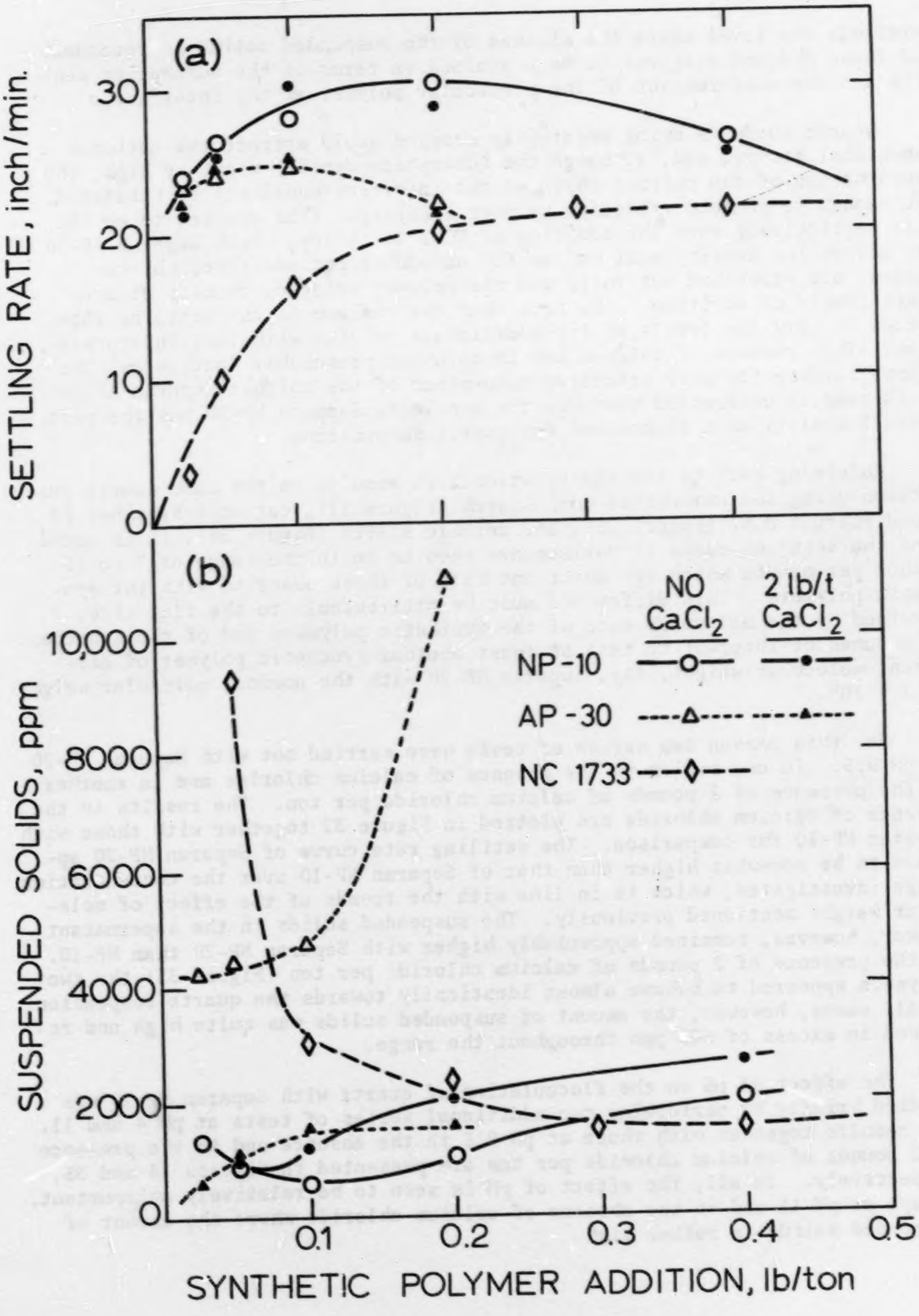


FIGURE 31. Flocculation Test Results on Quartz as a Function of Synthetic Polymer Addition at pH 9.5

parallels the level where the minimum of the suspended solids is recorded. All these phenomena appear to be explained in terms of the adsorption density and the conformation of the particular polymer at the interface.

Quartz surfaces being negatively charged would attract the cationic functional groups, and, although the adsorption density might be high, the conformation of the polymer chain at the interface would not be stretched out enough to promote effective polymer bridging. This appears to be the case particularly when the addition of NC 1773 is low. With Separan AP-30 the adsorption density must be low for an equivalent addition, but the chains are stretched out fully and the polymer bridging results at much lower levels of addition. The fact that the maximum in the settling rate occurs at very low levels of its addition is in line with this interpretation. The presence of calcium ion in solution presumably 'activates' the quartz surface for more effective adsorption of the anionic Separan AP-30. It is readily understood then why the non-ionic Separan NP-10 has the best overall quality as a flocculant for quartz suspensions.

Referring back to the flocculation test results on the same quartz suspension using the unmodified corn starch (Figure 11), cationic starches of two different D.S. (Figure 26), and anionic starch (Figure 28), it is noted that the settling rates at maximum are seen to be in the range of 7 to 15 inches per minute which are about one half of those observed with the synthetic polymers. This difference must be attributable to the floc size, governed by the molecular size of the synthetic polymers and of the starches. It becomes of interest to test at least another synthetic polymer of different molecular weight, say, Separan NP-20 with the nominal molecular weight of 2×10^6.

For this reason two series of tests were carried out with Separan NP-20 at pH 9.5: in one series in the absence of calcium chloride and in another in the presence of 2 pounds of calcium chloride per ton. The results in the absence of calcium chloride are plotted in Figure 32 together with those with Separan NP-10 for comparison. The settling rate curve of Separan NP-20 appears to be somewhat higher than that of Separan NP-10 over the concentration range investigated, which is in line with the trends of the effect of molecular weight mentioned previously. The suspended solids in the supernatant liquor, however, remained appreciably higher with Separan NP-20 than NP-10. In the presence of 2 pounds of calcium chloride per ton (Figure 33) the two polymers appeared to behave almost identically towards the quartz suspension. In all cases, however, the amount of suspended solids was quite high and remained in excess of 600 ppm throughout the range.

The effect of pH on the flocculation of quartz with Separan NP-10 was studied briefly by performing two additional series of tests at pH 4 and 11. The results together with those at pH 9.5 in the absence and in the presence of 2 pounds of calcium chloride per ton are presented in Figures 34 and 35, respectively. In all, the effect of pH is seen to be relatively unimportant. except at pH 11 and in the absence of calcium chloride where the amount of suspended solids is rather high.

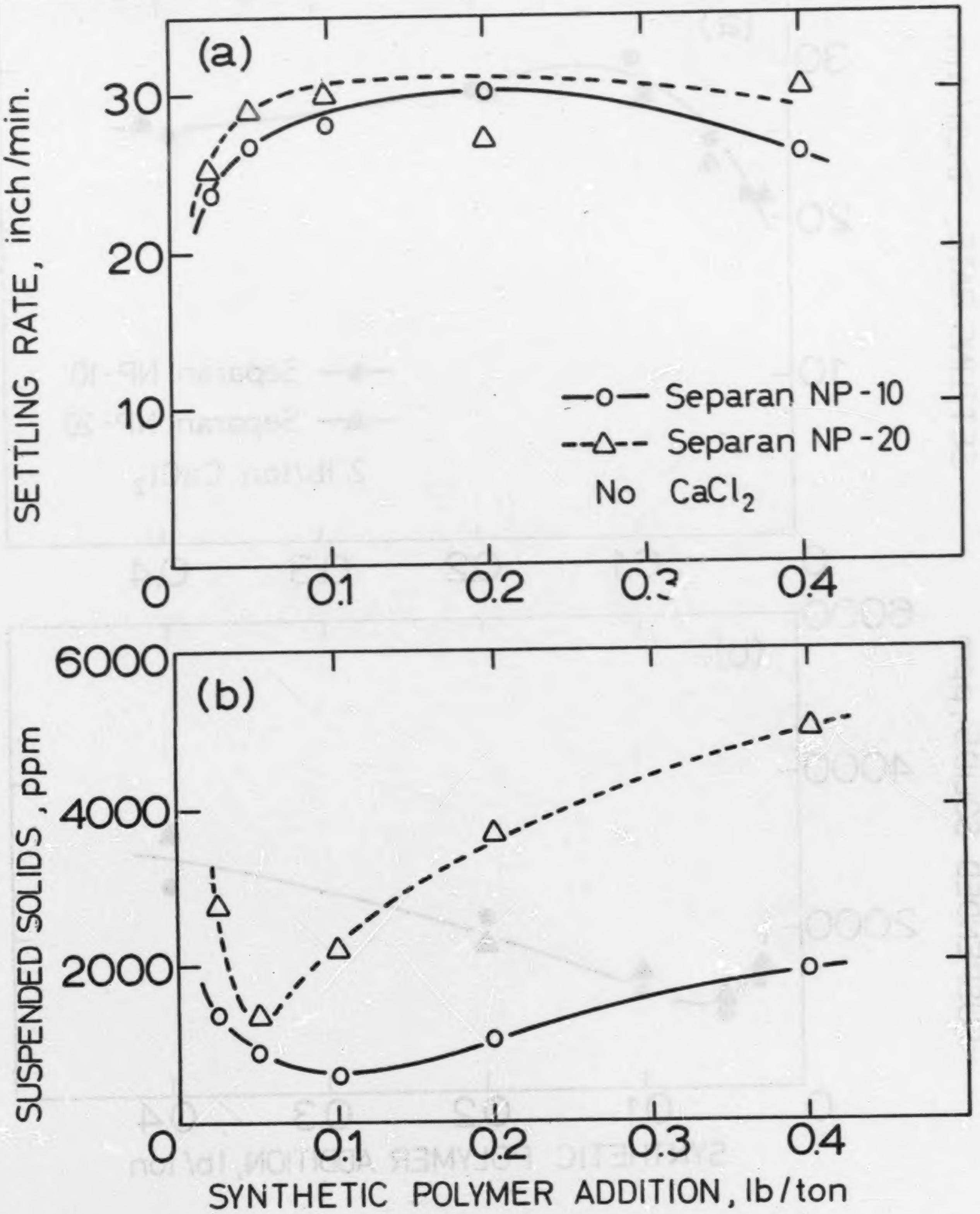


FIGURE 32. Flocculation Test Results on Quartz as a Function of Synthetic Polymer Addition at pH 9.5

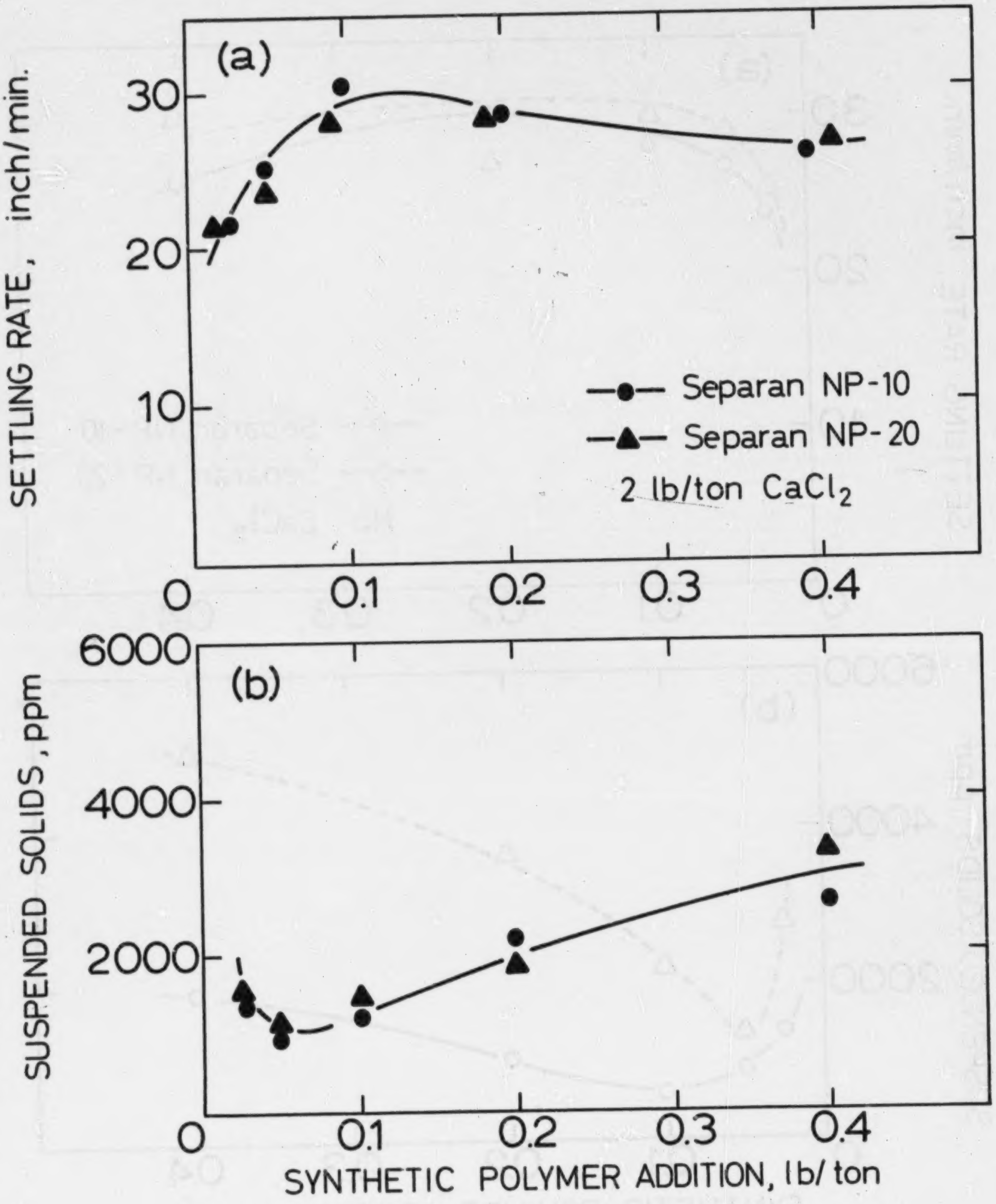


FIGURE 33. Flocculation Test Results on Quartz as a Function of Synthetic Polymer Addition at pH 9.5; Calcium Chloride 2 lb per ton

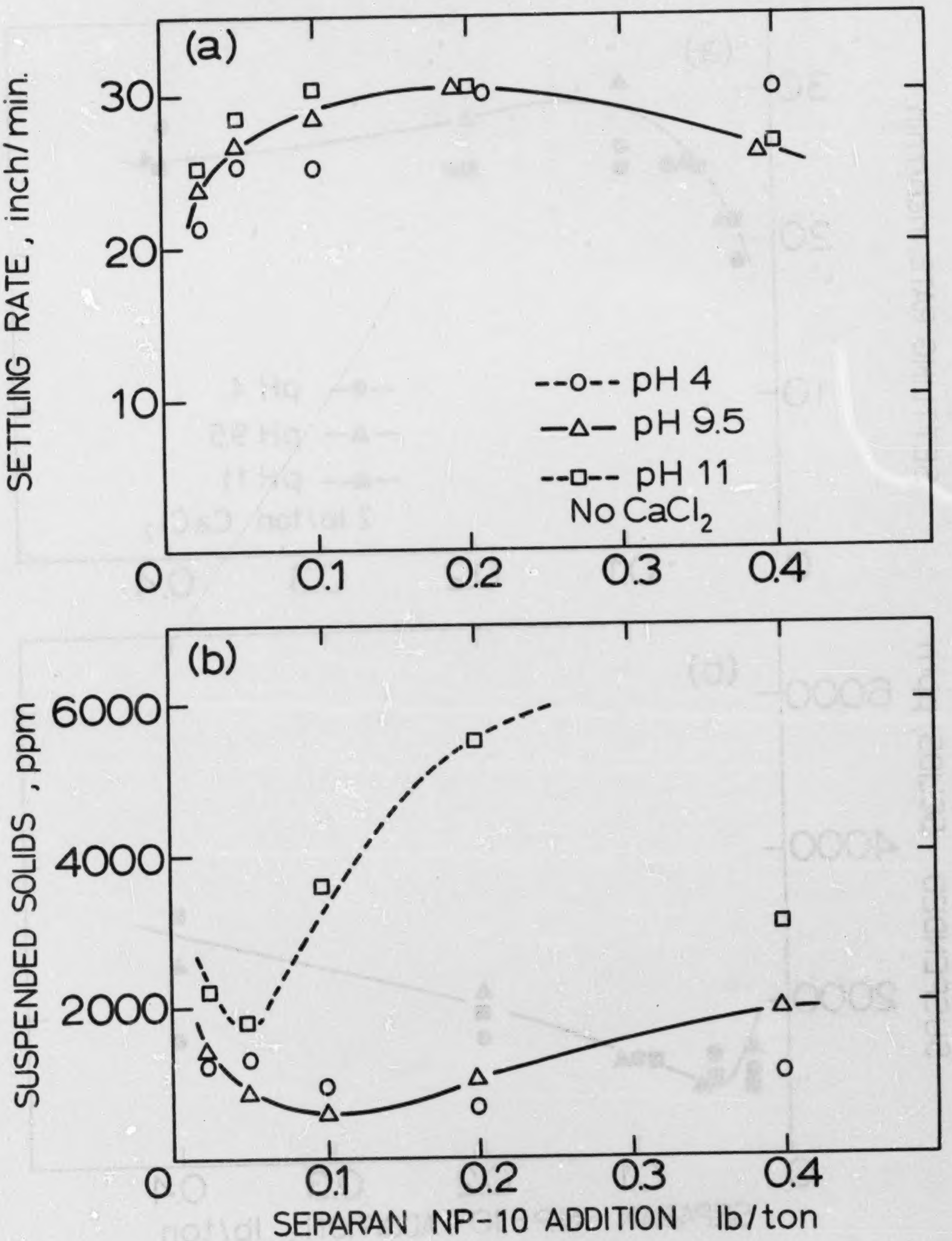


FIGURE 34. The Effect of pH on the Flocculation Test Results on Quartz as a Function of Separan NP-10 Addition

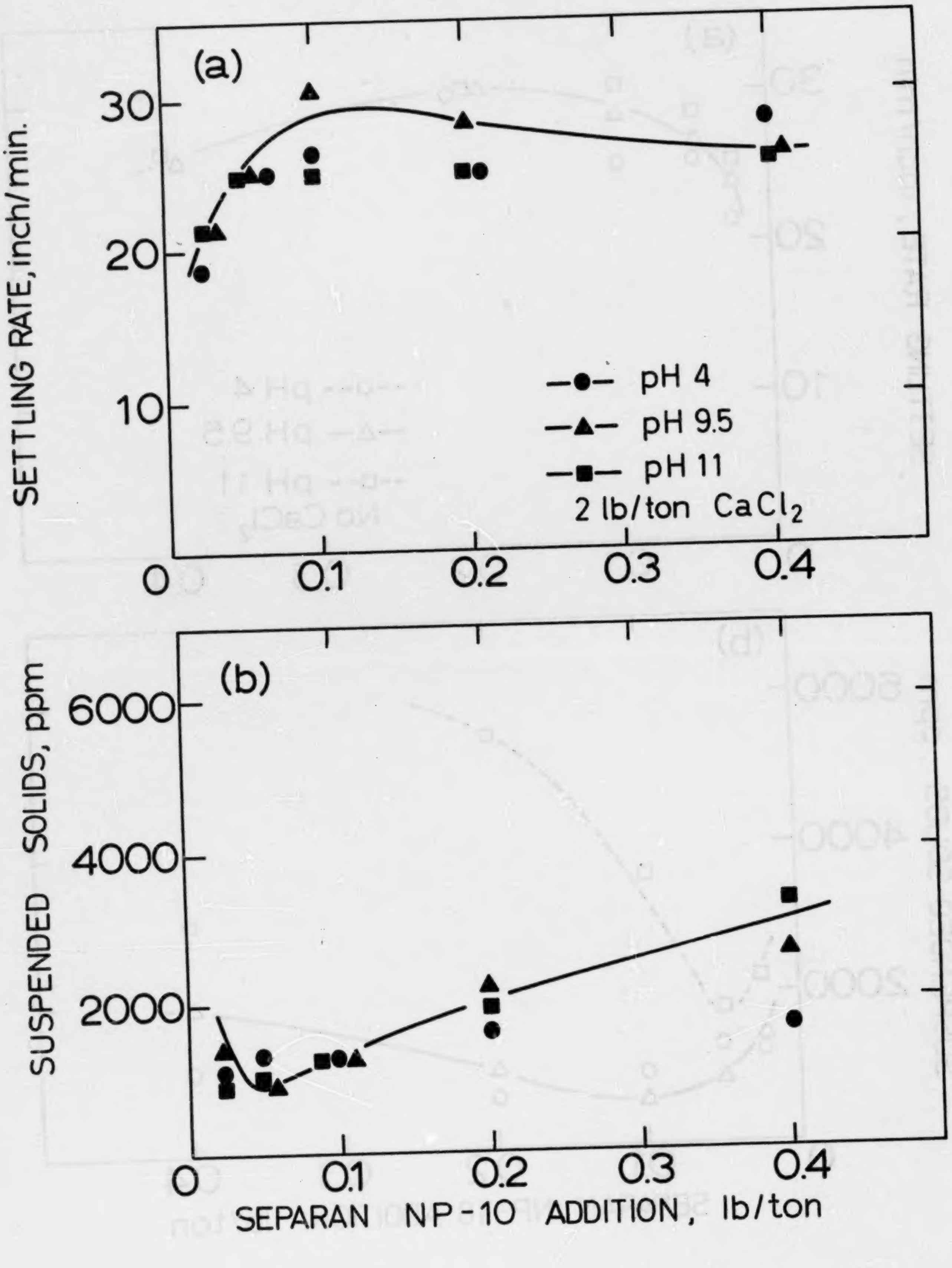


FIGURE 35. The Effect of pH on the Flocculation Test Results on Quartz as a Function of Separan NP-10 Addition; Calcium Chloride 2 lb per ton

Flocculation Tests on an Artificial Mixture of Quartz and Goethite

Two series of preliminary flocculation tests were performed on an artificial mixture of quartz and goethite. In one series an attempt was made to flocculate both the quartz and the goethite. The possibility of mutual flocculation of the two minerals and its effect on the settling rate and clarity were also explored. In the other series the selective flocculation of goethite and partial upgrading by desliming were tested.

Total Flocculation - Clarification

Destabilization of silica suspensions may be brought about by a proper choice of the concentration of an iron salt and of pH.[27] In the alkaline pH range a three-dimensional network formation due to the sorption of hydrolyzed iron (III) polymers was thought to be responsible for the particle aggregation. To ascertain if a mixture of quartz and goethite might result in an improvement of the flocculation behavior, particularly of quartz, a series of artificial mixtures of the two minerals with size moduli of 60 microns was prepared. The experimental conditionsselected were based on the information reported previously, namely, 50 grams of the artificial mixture per liter at pH 9.5, two pounds of calcium chloride per ton, and a level of corn starch addition proportioned to the ratio of quartz and goethite at their maximum settling rates. The corn starch level was shown to be 0.075 pound per ton for the quartz sample and 0.75 pound per ton for the goethite sample (Figure 19). The results thus obtained are shown in Figure 36(a). The experimental points, both of the settling rate and suspended solids, appear to be represented with lines convexly upwards, i.e., the settling rate of the mixture appears to have been accelerated by the presence of goethite, but the presence of goethite did not seem to affect the clarity of the supernatant water.

Previous tests have demonstrated that cationic starches are effective flocculants for both quartz and goethite and that cationic starches with high degrees of substitution are most efficacious (Figures 26 and 27). Similar tests were performed on a series of quartz and goethite mixtures under essentially identical conditions except for the omission of calcium chloride addition. For the flocculant,0.067 D.S. cationic starch was selected and the level of its addition was proportioned according to the ratio of the two minerals based on the condition observed at the maximum settling rates. These levels were 0.5 pound per ton for the quartz and 1.0 pound per ton for the goethite (Figures 26 and 27). The results are shown in Figure 36(b). It is apparent that the curve for the settling rate is convex upwards and that for the suspended solids concave upwards, showing that there is a beneficial effect of goethite on the flocculation of the quartz suspension.

Selective Flocculation - Desliming

In some of the flotation tests with the Mesabi iron ores the addition

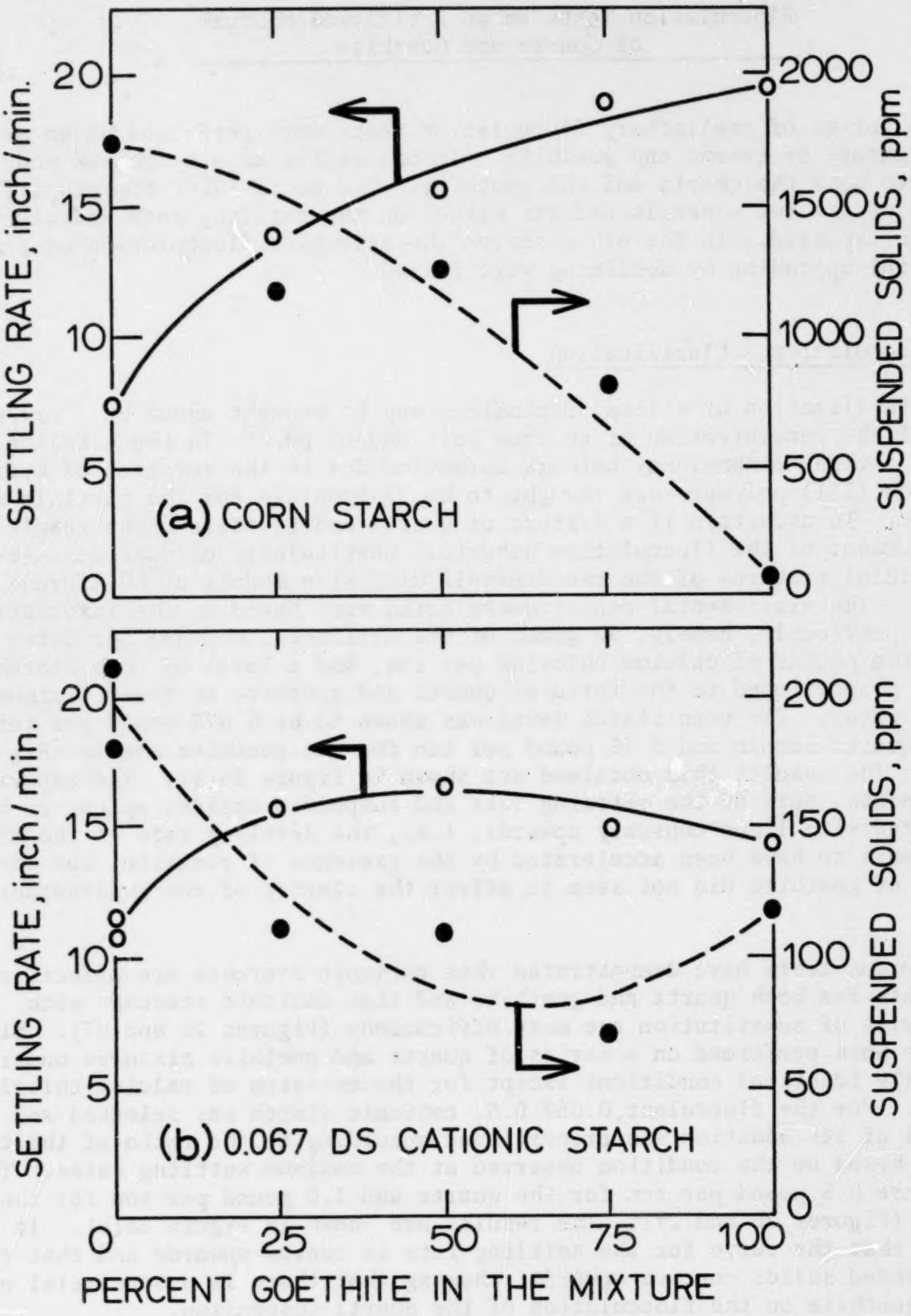


FIGURE 36. Flocculation Test Results on the Artificial Mixture of Goethite and Quartz (k=60μ) in various Proportions

(a) pH 9.5, $CaCl_2$ 2 lb per ton, and Corn Starch 0.075 to 0.75 lb per ton

(b) pH 9.5, 0.067 DS Cationic Starch 0.5 to 1.0 lb per ton of causticized corn starch was observed to result in two relatively well-defined layers of sediment upon standing.[9] In the present investigation it was shown that goethite can be flocculated with corn starch in the absence of calcium ion whereas quartz cannot. It appears, therefore, that goethite may be selectively flocculated with corn starch and that quartz particles remaining in suspension may be removed by decantation. Based on the results presented in Figures 10, 13, and 14 the test conditions were selected as follows. Fifty grams of an artificial mixture of goethite and quartz samples with a size modulus of 60 microns was placed in a 1000-ml graduated cylinder and diluted with make-up water to near the 1000-ml mark so that the subsequent addition of reagent would give a total pulp volume of 1000 ml. At this point the pH of the pulp was adjusted either with sodium hydroxide or hydrochloric acid, which was followed by the addition of starch in three equal portions, mixing being performed between each addition by gently inverting the cylinder three times between each addition. After the final addition of starch, the cylinder was inverted five times and set down. The settling of the goethite and quartz mixture began immediately. After one minute the mud line had reached the bottom. The tip of a siphon was then lowered to the 900-ml mark and the supernatant water above the mark was siphoned off. Another 900 ml of water, whose pH had been preadjusted to the same value, was added to the remaining solids. The cylinder was inverted five times, set down, and the settling and siphoning procedure was repeated. The desliming process was performed six times.

Initially, a series of three tests was carried out to explore the effect of the pulp pH by keeping the level of starch addition constant at 0.375 pound per ton: the first at natural near neutral pH, the second at pH 9.5, and the third at pH 11. The weights of each slime fraction and their analytical results are presented in Table 9, Sections A, B, and C, and are depicted in Figure 37(a), in which the percent iron recovery in the sand fraction is plotted against the percent iron in the sand fraction. The vertical line at 28.3 percent iron shows the line of no selectivity. The experimental curves extend markedly towards higher grades of the sand fraction, indicating the selectivity of the desliming operation. As seen in the figure, the grade-recovery curves are displaced further to the right as the pulp pH is raised indicating that the selective desliming operation is reasonable since the quartz suspensions are known to become stable and difficult to clarify after an exposure to the alkaline medium. Though this condition assists the selectivity of the desliming operation, a rather serious problem may be anticipated when the water is to be recycled or to be released from the plant. It is also noted in the curves at pH 9.5 and 11 that after about three decantations the line tends to become steeper indicating no effective upgrading is obtained through further desliming.

The effect of the level of starch addition was investigated next in a series of tests at pH 9.5. A control test was performed without the starch addition. The test results are given in Table 9, Sections D, E, and F, and depicted in Figure 37(b). It is readily apparent that in the absence of the starch there is no selectivity in the desliming operation. In fact, the experimental curve slopes towards lower grades of the sand fraction somewhat, indicating the reversal in the selectivity of the separation. With the ad-

TABLE 9. SELECTIVE FLOCCULATION AND PARTIAL UPGRADING RESULTS ON AN ARTIFICIAL MIXTURE OF GOETHITE AND QUARTZ (k = 60μ)

			Slime Fraction			Sand Fraction		
	% Wt	% Fe	Cum % Wt	Cum % Fe	Cum Fe Rec	Cum % Wt	Cum % Fe	Cum Fe Rec
A. pH ∼ 7; Corn Starch 0.375 lb/ton								
1st Desliming	3.06	2.09	3.06	2.09	0.22	96.94	29.44	99.78
2nd Desliming	2.30	8.97	5.36	5.04	0.94	94.64	29.94	99.06
3rd Desliming	2.01	13.85	7.37	7.45	1.92	92.63	30.29	98.08
4th Desliming	1.64	17.23	9.01	9.23	2.91	90.99	30.53	97.09
5th Desliming	1.44	19.88	10.45	10.69	3.91	89.55	30.70	96.09
6th Desliming	1.45	22.62	11.90	12.15	5.05	88.10	30.83	94.95
Sand	88.10	30.83						
Composite	100.00	28.61						
B. pH 9.5; Corn Starch 0.375 lb/ton								
1st Desliming	7.63	4.97	7.63	4.97	1.35	92.37	30.04	98.65
2nd Desliming	10.27	4.11	17.90	4.48	2.85	82.10	33.29	97.15
3rd Desliming	8.94	9.74	26.84	6.23	5.94	73.16	36.16	94.06
4th Desliming	5.24	24.95	32.08	9.29	10.59	67.92	37.03	89.41
Sand	67.92	37.03						
Composite	100.00	28.13						
C. pH 11; Corn Starch 0.375 lb/ton								
1st Desliming	21.11	4.59	21.11	4.59	3.41	78.89	34.79	96.59
2nd Desliming	10.94	6.76	32.05	5.33	6.01	67.95	39.31	93.99
3rd Desliming	5.09	16.54	37.14	6.87	8.97	62.86	41.15	91.02
4th Desliming	3.92	32.20	41.06	9.29	13.42	58.94	41.74	86.58
5th Desliming	3.80	40.89	44.86	11.96	18.88	55.14	41.80	81.12
6th Desliming	3.36	45.41	48.22	14.29	24.25	51.78	41.57	75.75
Sand	51.78	41.57						
Composite	100.00	28.42						

TABLE 9. (CONTINUED)

			Slime Fraction			Sand Fraction		
	% Wt	% Fe	Cum % Wt	Cum % Fe	Cum Fe Rec	Cum % Wt	Cum % Fe	Cum Fe Rec
D. pH 9.5; Corn Starch None								
1st Desliming	20.13	32.48	20.13	32.48	22.95	79.87	27.48	77.05
2nd Desliming	4.65	32.16	24.78	32.42	28.20	75.22	27.19	71.80
3rd Desliming	1.40	32.64	26.18	32.43	29.81	73.82	27.09	70.19
4th Desliming	0.65	32.06	26.83	32.42	30.54	73.17	27.04	69.46
5th Desliming	0.36	31.41	27.19	32.41	30.93	72.81	27.02	69.07
6th Desliming	0.47	28.85	27.66	32.35	31.41	72.34	27.01	68.59
Sand	72.34	27.01						
Composite	100.00	28.49						
E. pH 9.5; Corn Starch 0.1 lb/ton								
1st Desliming	23.84	11.99	23.84	11.99	10.16	76.16	33.18	89.84
2nd Desliming	10.54	31.87	34.38	18.08	22.10	65.62	33.39	77.90
3rd Desliming	4.97	46.69	39.35	21.70	30.35	60.65	32.30	69.65
4th Desliming	3.75	49.23	43.10	24.09	36.91	56.90	31.19	63.09
5th Desliming	3.02	49.18	46.12	25.74	42.19	53.88	30.18	57.81
6th Desliming	1.49	49.84	47.61	26.49	44.83	52.39	29.62	55.17
Sand	52.39	29.62						
Composite	100.00	28.13						
F. pH 9.5; Corn Starch 0.65 lb/ton								
1st Desliming	14.95	2.54	14.95	2.54	1.34	85.05	32.88	98.66
2nd Desliming	9.11	2.66	24.06	2.59	2.19	75.94	36.51	97.81
3rd Desliming	5.89	5.88	29.95	3.23	3.42	70.05	39.09	96.58
4th Desliming	3.61	9.02	33.56	3.86	4.56	66.44	40.72	95.44
5th Desliming	2.98	16.18	36.54	4.86	6.27	63.46	41.87	93.73
6th Desliming	2.51	20.77	39.05	5.88	8.10	60.95	42.74	91.90
Sand	60.95	42.74						
Composite	100.00	28.35						

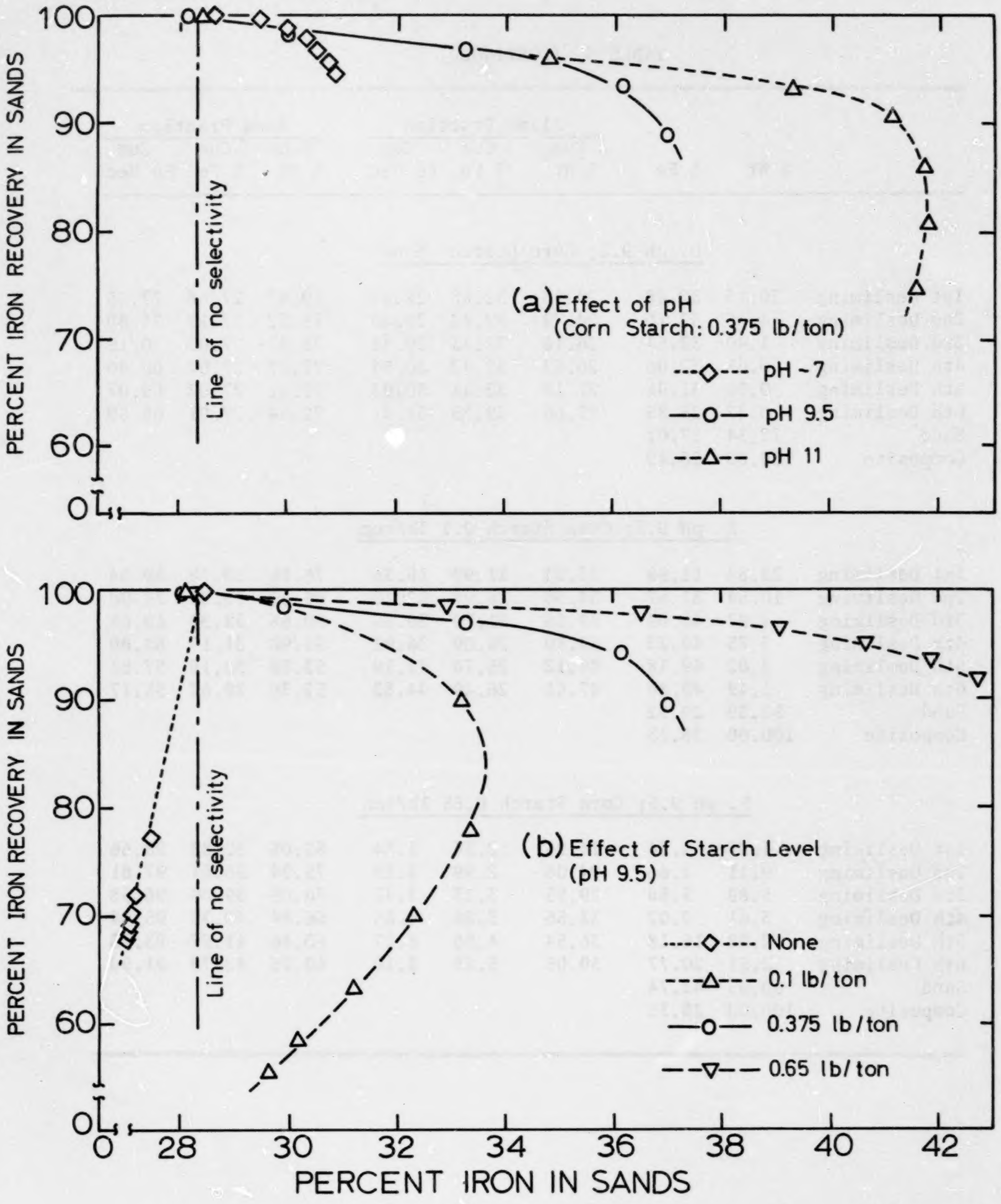


FIGURE 37. Selective Flocculation and Partial Upgrading Results on an Artificial Mixture of Goethite and Quartz (k=60μ); (a) Effect of pH at a Constant Starch Level of 0.375 lb per ton, (b) Effect of the Level of Starch Addition at pH 9.5

dition of the starch, the curves extend towards higher grades of the sand fraction. The higher the level of the starch addition, the further the shift of the grade-recovery curves to the right. This again is in good agreement with the test results on single mineral systems; a quartz suspension cannot be flocculated with starch in the absence of calcium ion. It becomes of interest to investigate the effect of calcium ion in solution, which is inevitably present in all the iron ores and causes quartz particles to flocculate in the high pH region.

Zeta-Potential Measurements

Zeta potentials of goethite and quartz in the absence and in the presence of corn starch and/or calcium chloride at different pH were determined by the streaming-potential measurement technique. To compare the electrokinetic behavior of the ground samples of St. Peter sand and Brazilian quartz, which were too fine to apply the above method, the electrophoretic mobility measurement technique was used. The results are reported under the headings of goethite and quartz.

Zeta Potential of Goethite

Figure 38 shows the zeta potential of goethite as a function of corn starch at neutral pH and at pH 10.7. Both curves show the same trend--much of the change in the zeta potential occurs when the starch concentration is less than 10 mg per liter. This is in good agreement with the adsorption isotherms of the same starch on both quartz and hematite.[15] The abstraction at low levels of addition is nearly complete, resulting in a steep rise in the adsorption density, and then approaches saturation coverage corresponding to a particular pH of the solution (Figure 51). The zeta potentials in the plateau region correspond to the adsorption densities at the saturation coverages.

Marked difference in the zeta potential in the plateau region at the two pH values appears to provide an implication on the conformation of starch molecules on the goethite surface. When the goethite sample was equilibrated with a solution containing 50 mg of starch per liter at pH 10.7, the zeta potential was highly negative and was about -33 mV. Lowering of the solution pH, but maintaining the constant starch concentration of 50 mg per liter, however, resulted in the decrease in the zeta potential approaching a plateau of about -8 mV in the near neutral pH as shown in Figure 39. This value of zeta potential corresponds to that at pH 6.7 in Figure 38. When the direction of the pH change is reversed, but at a starch concentration of 50 mg per liter, the zeta potential increases only to a range of -10 to -12 mV. This hysteresis effect may be readily understood if the irreversibility of the starch adsorption is assumed. The zeta potential values of the "increasing pH" cycle may represent those of the adsorbed starch itself. The starch molecules adsorbed from the high-pH solution must be highly stretched, and the zeta potential observed at that pH appears to be influenced by the highly negative surface of goethite. The adsorption density

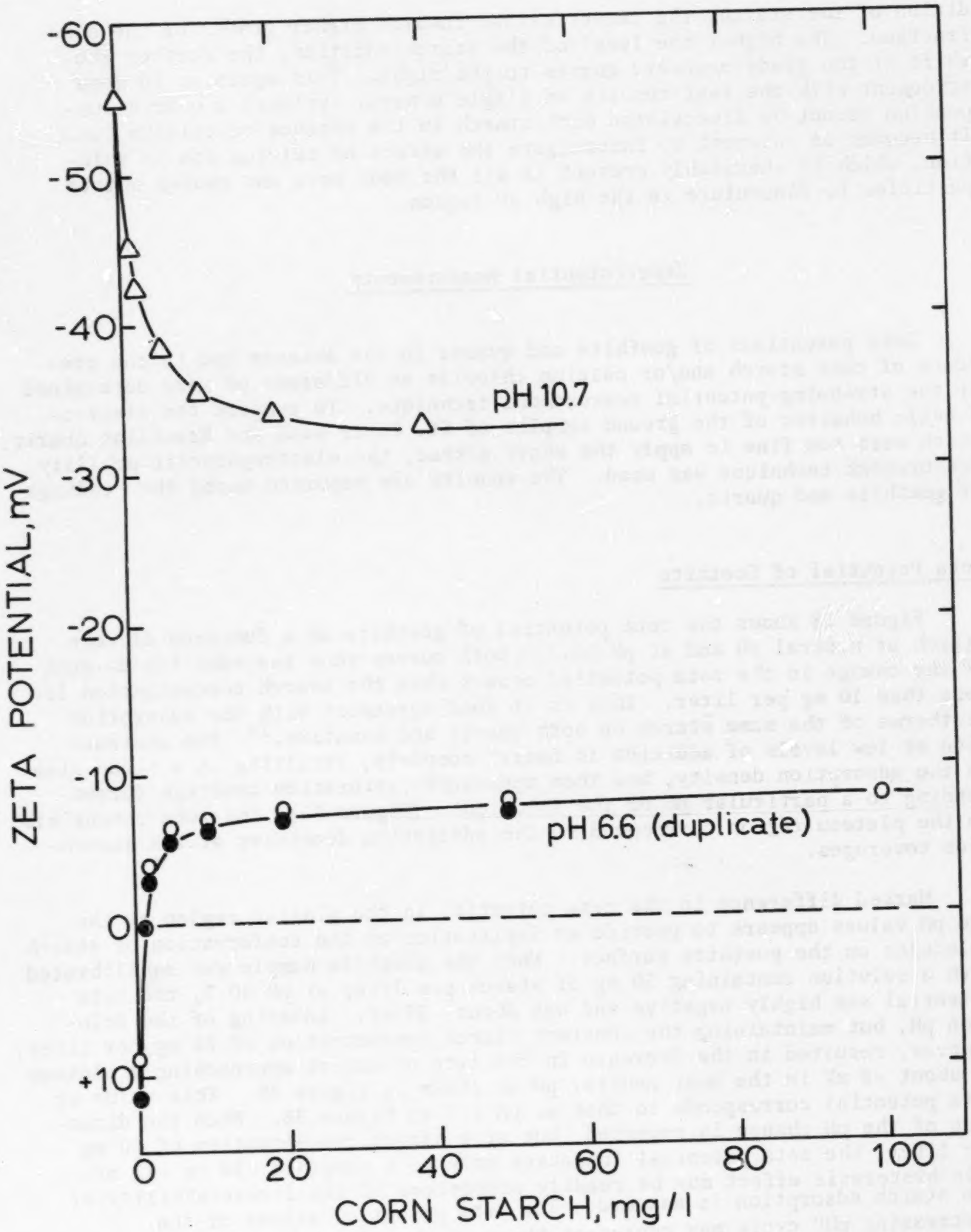


FIGURE 38. Zeta Potential of Goethite as a Function of Corn Starch Concentration

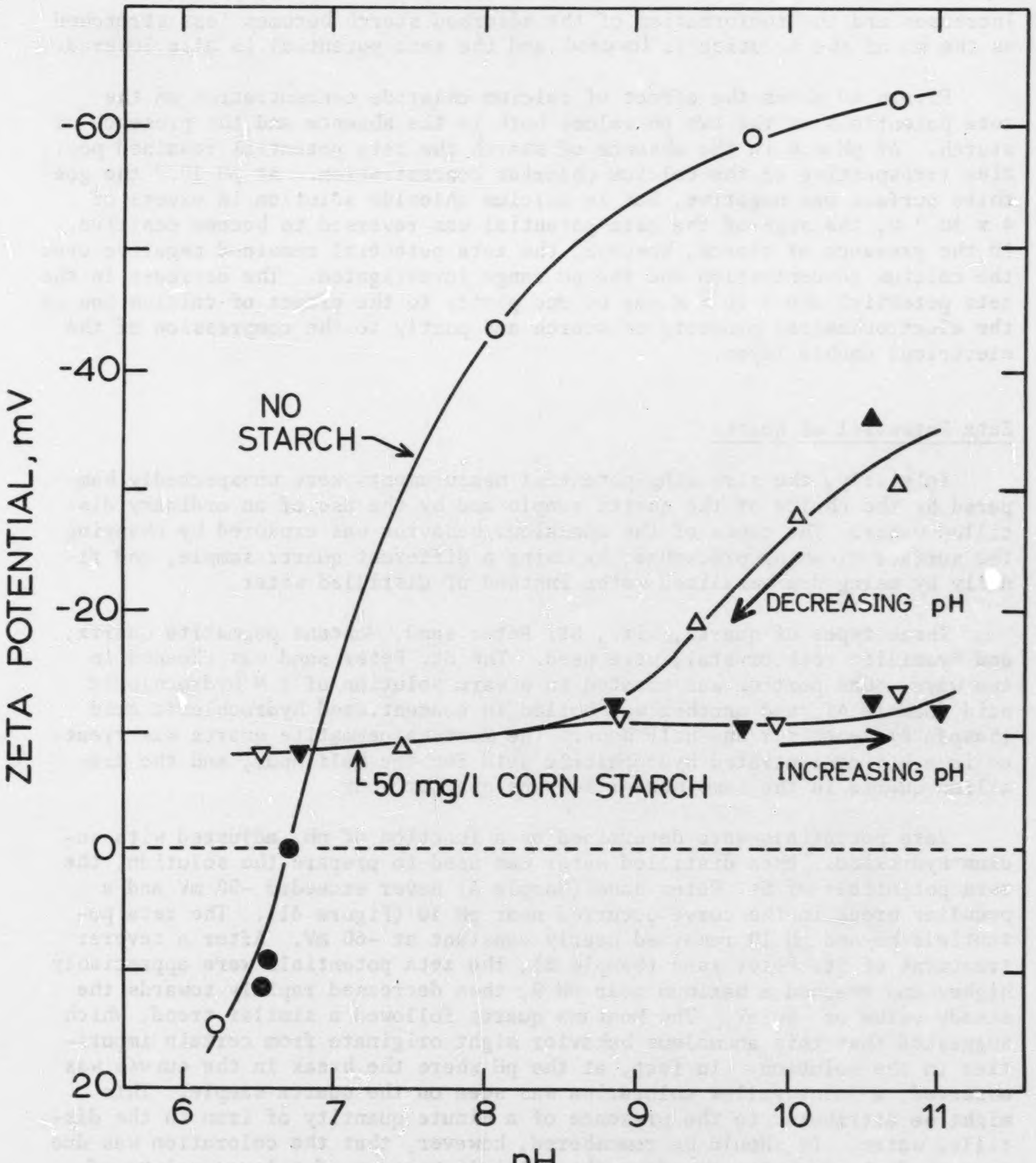


FIGURE 39. Zeta Potential of Goethite as a Function of pH in the Absence and in the Presence of 50 mg of Corn Starch per Liter

increases and the conformation of the adsorbed starch becomes less stretched as the pH of the solution is lowered and the zeta potential is also lowered.

Figure 40 shows the effect of calcium chloride concentration on the zeta potentials at the two pH values both in the absence and the presence of starch. At pH 6.6 in the absence of starch the zeta potential remained positive irrespective of the calcium chloride concentration. At pH 10.7 the goethite surface was negative, but in calcium chloride solution in excess of 4×10^{-4} M, the sign of the zeta potential was reversed to become positive. In the presence of starch, however, the zeta potential remained negative over the calcium concentration and the pH range investigated. The decrease in the zeta potential above 10^{-5} M may be due partly to the effect of calcium ion on the electrochemical property of starch and partly to the compression of the electrical double layer.

Zeta Potential of Quartz

Initially, the streaming-potential measurements were unexpectedly hampered by the choice of the quartz sample and by the use of an ordinary distilled water. The cause of the anomalous behavior was explored by changing the surface cleaning procedure, by using a different quartz sample, and finally by using demineralized water instead of distilled water.

Three types of quartz, viz., St. Peter sand, Montana pegmatite quartz, and Brazilian rock crystal, were used. The St. Peter sand was cleaned in two ways. One portion was treated in a warm solution of 1 N hydrochloric acid (Sample A), and another was boiled in concentrated hydrochloric acid (Sample B), each for one-half hour. The Montana pegmatite quartz was treated in a hot concentrated hydrochloric acid for one-half hour, and the Brazilian quartz in the same manner for one-quarter hour.

Zeta potentials were determined as a function of pH, adjusted with sodium hydroxide. When distilled water was used to prepare the solution, the zeta potentials of St. Peter sand (Sample A) never exceeded -90 mV and a peculiar break in the curve occurred near pH 10 (Figure 41). The zeta potentials beyond pH 10 remained nearly constant at -60 mV. After a severer treatment of St. Peter sand (Sample B), the zeta potentials were appreciably higher and reached a maximum near pH 9, then decreased rapidly towards the steady value of -60 mV. The Montana quartz followed a similar trend, which suggested that this anomalous behavior might originate from certain impurities in the solution. In fact, at the pH where the break in the curves was observed, a faint yellow coloration was seen on the quartz sample. This might be attributed to the presence of a minute quantity of iron in the distilled water. It should be remembered, however, that the coloration was due to a gradual accumulation after the multiple passage of a large volume of the solution during the streaming-potential measurements.

In order to check this particular point the measurements were carried out on the Montana pegmatite quartz and the Brazilian quartz, using demineralized water. For the Brazilian quartz the measurements were replicated

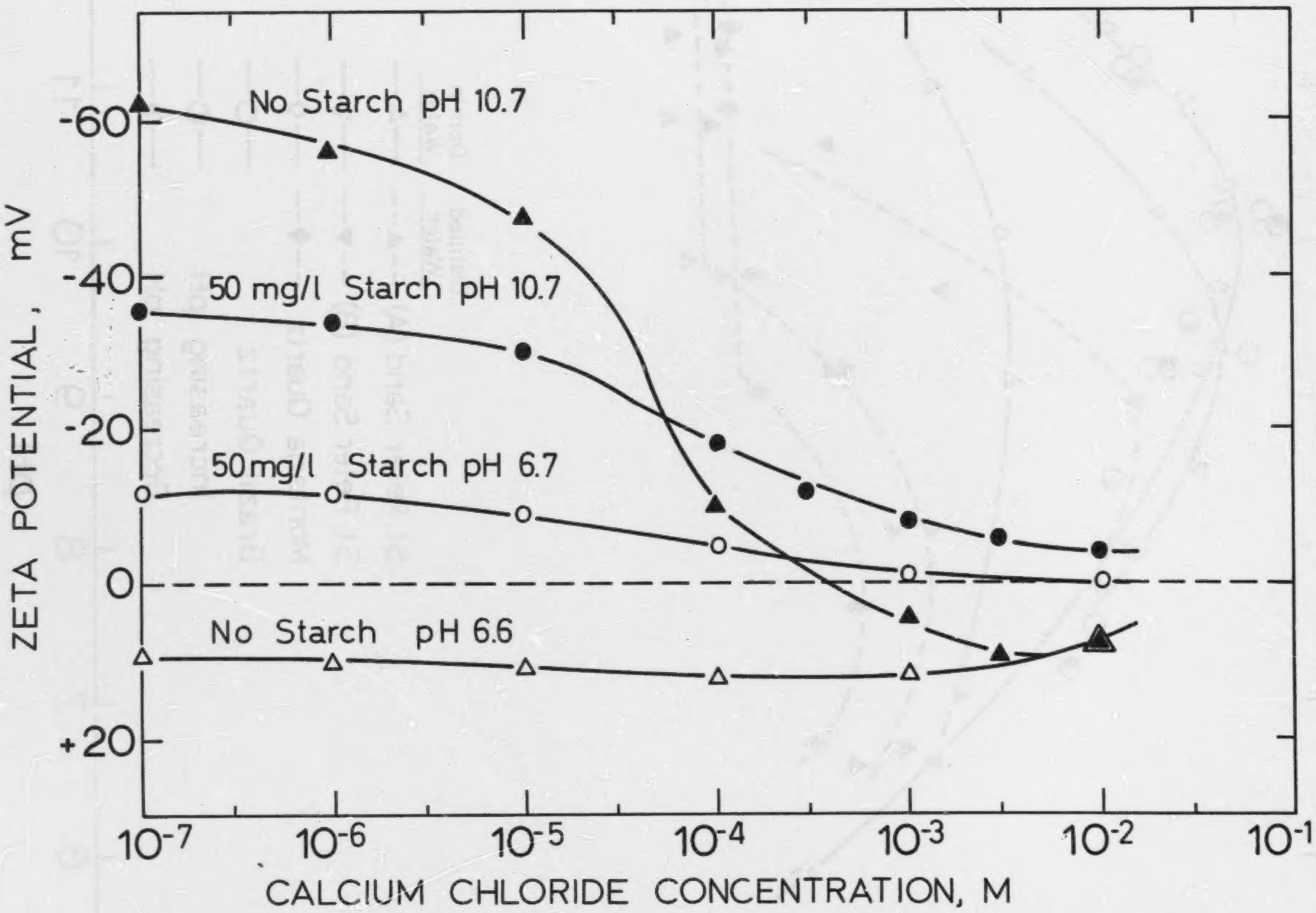


FIGURE 40. Zeta Potential of Goethite as a Function of Calcium Chloride Concentration in the Absence and in the Presence of 50 mg of Corn Starch per Liter

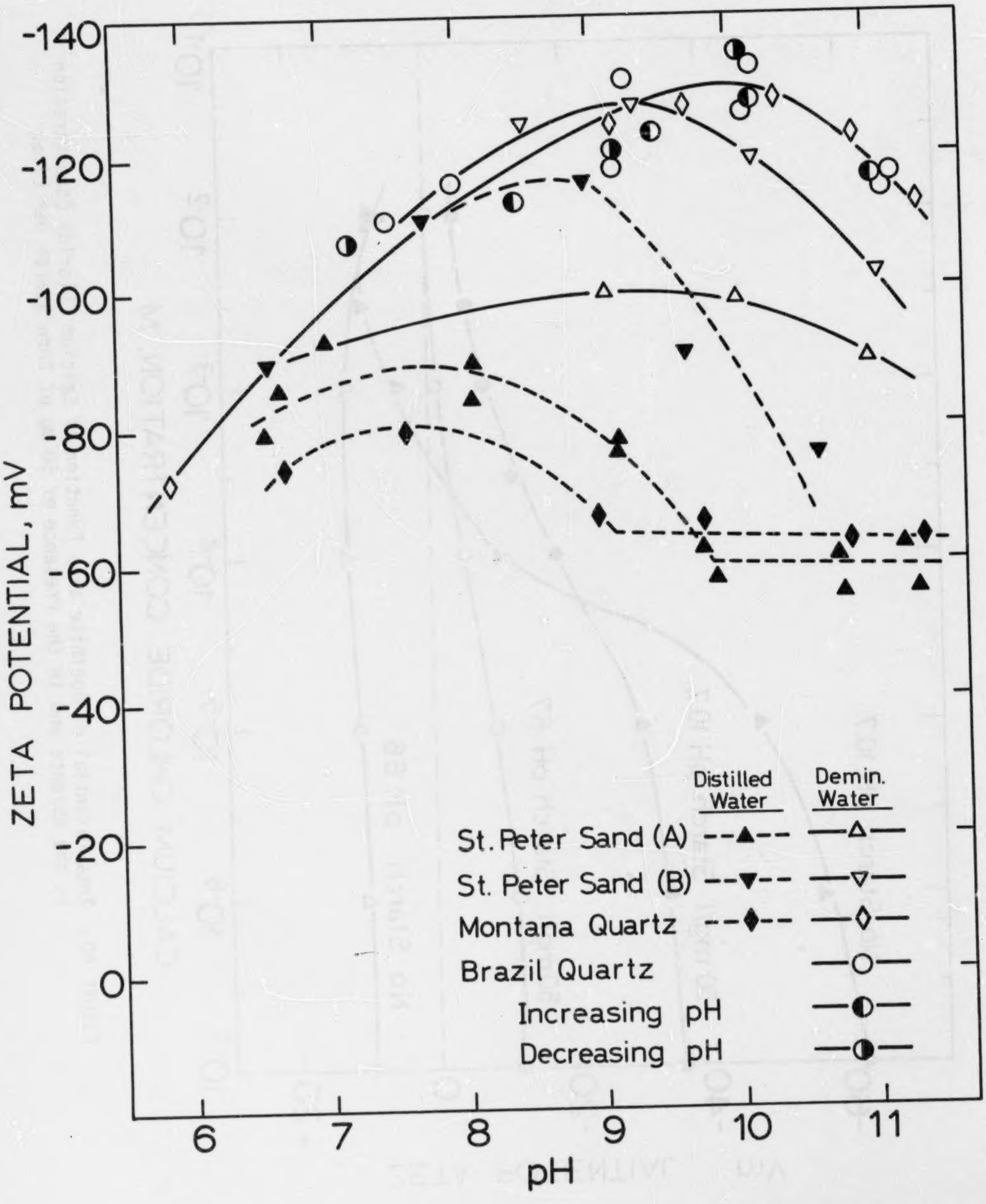


FIGURE 41. Comparison of Zeta Potentials of Various Quartz Samples as a Function of pH in Distilled and Demineralized Water

a few times, once completing a cycle of increasing the pH and then decreasing the pH on an identical sample for a hysteresis effect. All the results are plotted in Figure 41 together with those obtained in distilled water for comparison. It is readily apparent that the general shapes of the zeta-potential curves in demineralized water are quite different from those obtained in distilled water, and that the data of the Montana pegmatite quartz and those of Brazilian quartz are in good agreement. In fact, the present results with the Brazilian quartz are virtually identical to those reported in literature on the quartz sample from the same source and conductivity water.[11] Furthermore, the zeta potentials of the increasing pH cycle, indicating the absence of the hysteresis effect.

The difference between Samples A and B of St. Peter sand in demineralized water might be attributed to the presence of a minor quantity of impurities present on the original sand grains which was removed by boiling the sand in concentrated hydrochloric acid. It becomes of interest to compare the zeta potentials of a finely ground St. Peter sand with that of Brazilian quartz using an electrophoresis technique. Here the freshly fractured surfaces of different quartz samples may be compared. Furthermore, when a quartz sample is ground fine and a limited amount of distilled water is used, the effect of a minor quantity of impurities present in distilled water might become negligible.

In order to ascertain this particular point, the electrophoretic mobilities of ground samples of St. Peter sand dispersed both in distilled and in demineralized water were determined as functions of pH. The results were then compared with the electrophoretic mobilities of ground Brazilian quartz in demineralized water. During the course of the experimental work it was noted that the electrophoretic mobility increased gradually with time. It appeared that the suspension in demineralized water required the longest period, extending from a few days for the moderately alkaline solution to well over a week for others. Three series of determinations were made to test the reproducibility of each condition. The results are plotted in Figure 42(a). Although the scatter of the experimental points is relatively small within each series of determinations, the curves appear to be displaced vertically depending on the concentration of the suspended solids; the thinner the suspension, the higher the mobility. Nevertheless, all the points corresponding to the three sets of conditions are seen to scatter about a line drawn through the experimental points, indicating that the electrophoretic mobility of quartz does not depend on the types of quartz or on the kind of water used. Furthermore, it is noted that, unlike the streaming potentials shown in Figure 41, above a pH of 9 in distilled water the electrophoretic mobility did not decrease.

The mobility data were then converted to the zeta-potential values using two limiting cases[22] of the von Smoluchowski and Hückel equations. In Figure 42(b) the zeta-potential values calculated on the basis of Hückel's treatment (with a factor of 6) are plotted. A broken-line curve was drawn through the plotted values. The same curve, but corresponding to the other limiting case of von Smoluchowski's treatment (with a factor of 4) was drawn with a dotted line. It is readily apparent that the former is in closer agreement with the zeta-potential curves of the Brazilian quartz and of the

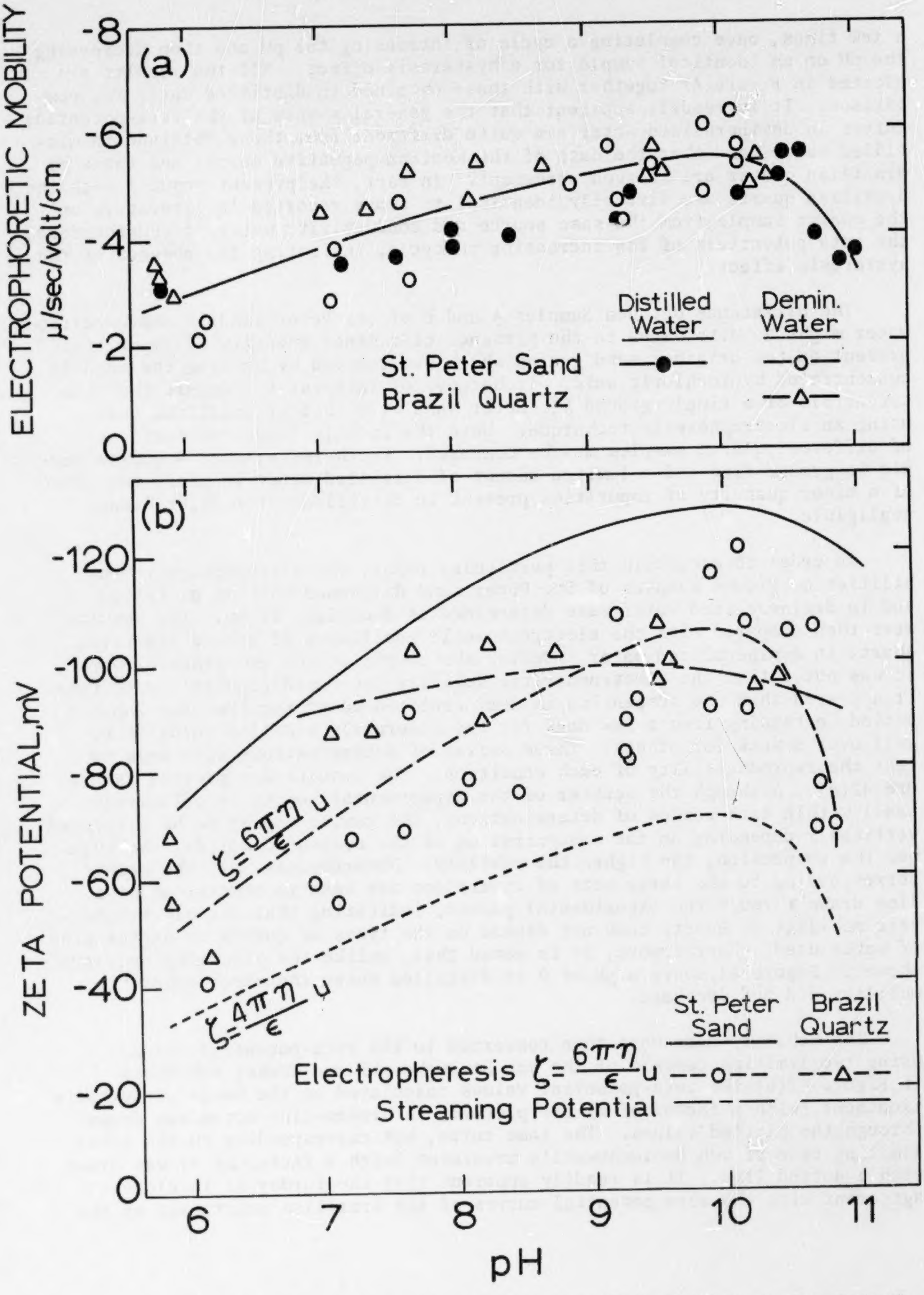


FIGURE 42. Electrophoretic Mobility and Zeta Potential of a Ground St. Peter Sand and a Brazilian Quartz as a Function of pH

St. Peter sand, Sample B, in demineralized water, determined by the streaming-potential technique. This was, more or less, to be expected since the particles observed in the measurements were extremely small.

To further confirm the effect of using distilled and demineralized water on the flocculation behavior of quartz, a few tests were performed at pH 9.5 and 11.5 under corresponding conditions. Both the settling rates and the amount of suspended solids in supernatant liquor were compared. Again, presumably to the large surface area of the quartz sample and the relatively small quantity of water used in the flocculation tests, the flocculation behavior was hardly affected by the type of water used.

Having ascertained that Brazilian quartz in demineralized water behaved satisfactorily, the effects of corn starch, calcium chloride, and pH on the zeta potentials were investigated. Figure 43 shows the effect of corn starch on the zeta potentials at three pH values in the absence of calcium chloride. The zeta potentials both at pH 9.5 and 11.1 are affected very little by the presence of corn starch, which is in line with the adsorption data that the adsorption density of corn starch on quartz is extremely small. At pH 5, however, the zeta potential decreases as the concentration of the starch is increased, more or less, contrary to that at pH 9.5 or 11.1. This behavior is indicative of some adsorption of the starch at this pH. In fact, the adsorption of starch on quartz is known to increase as the pH is decreased.[15]

The effect of pH on the zeta potentials of Brazilian quartz in the presence of 50 mg of corn starch per liter was determined, and the results are presented in Figure 44 together with those in the absence of starch. The pH of the solution was adjusted using either hydrochloric acid or sodium hydroxide. In the absence of starch the zeta potential is seen to remain negative in the pH range from 2 to 11, indicating that the point-of-zero-charge of quartz is located at a pH below 2. This observation is in agreement with the results reported by Li and de Bruyn.[12]

In the presence of starch the zeta potentials were lowered somewhat over the pH range investigated. In the alkaline pH range the experimental points determined in the direction of increasing pH and of decreasing pH are seen to be nearly coincident, indicating that the hysteresis effect observed on goethite is absent on quartz in this pH range due presumably to rather low adsorption of the starch molecules, In the acid range, however, the zeta potentials of increasing pH are seen to be appreciably lower than those of decreasing pH, showing, more or less, the same trend as observed on goethite.

Figure 45 shows the effect of calcium chloride concentration on the zeta potentials at four pH values in the absence of corn starch. It is interesting to note that the zeta potentials remained negative at pH 4 and near 7, irrespective of calcium chloride concentration, but at pH 9.5 and in a solution of calcium chloride exceeding 10^{-2} M the sign of the zeta potential on the quartz was reversed to become positive. At pH 11 the solution concentration of calcium chloride, at which the sign of the zeta potential is reversed is seen to be considerably lower than 10^{-2} M, and is estimated at 2.5×10^{-3} M. The zeta potentials under identical conditions, but in the

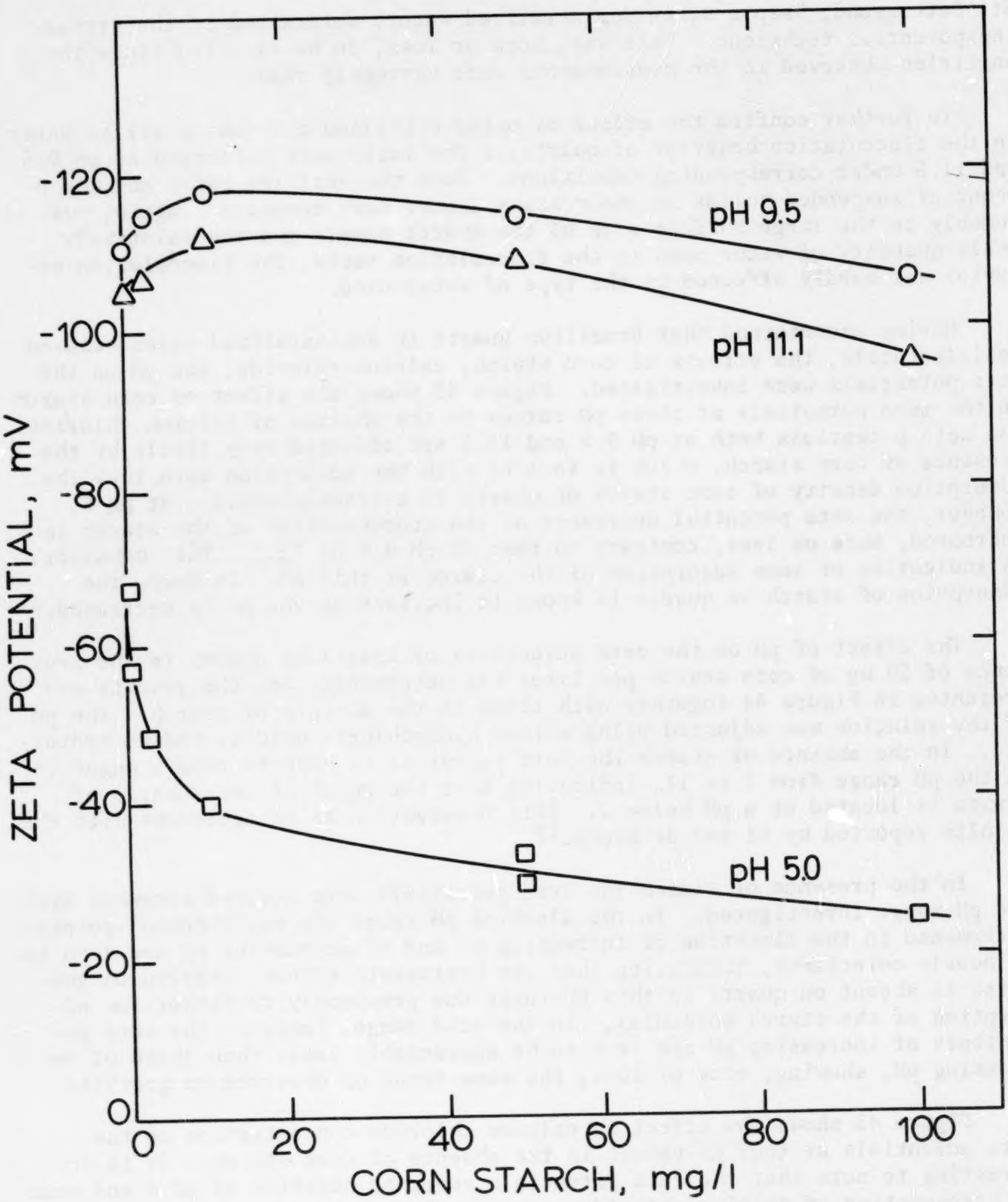


FIGURE 43. Zeta Potential of Brazilian Quartz as a Function of Corn Starch Concentration

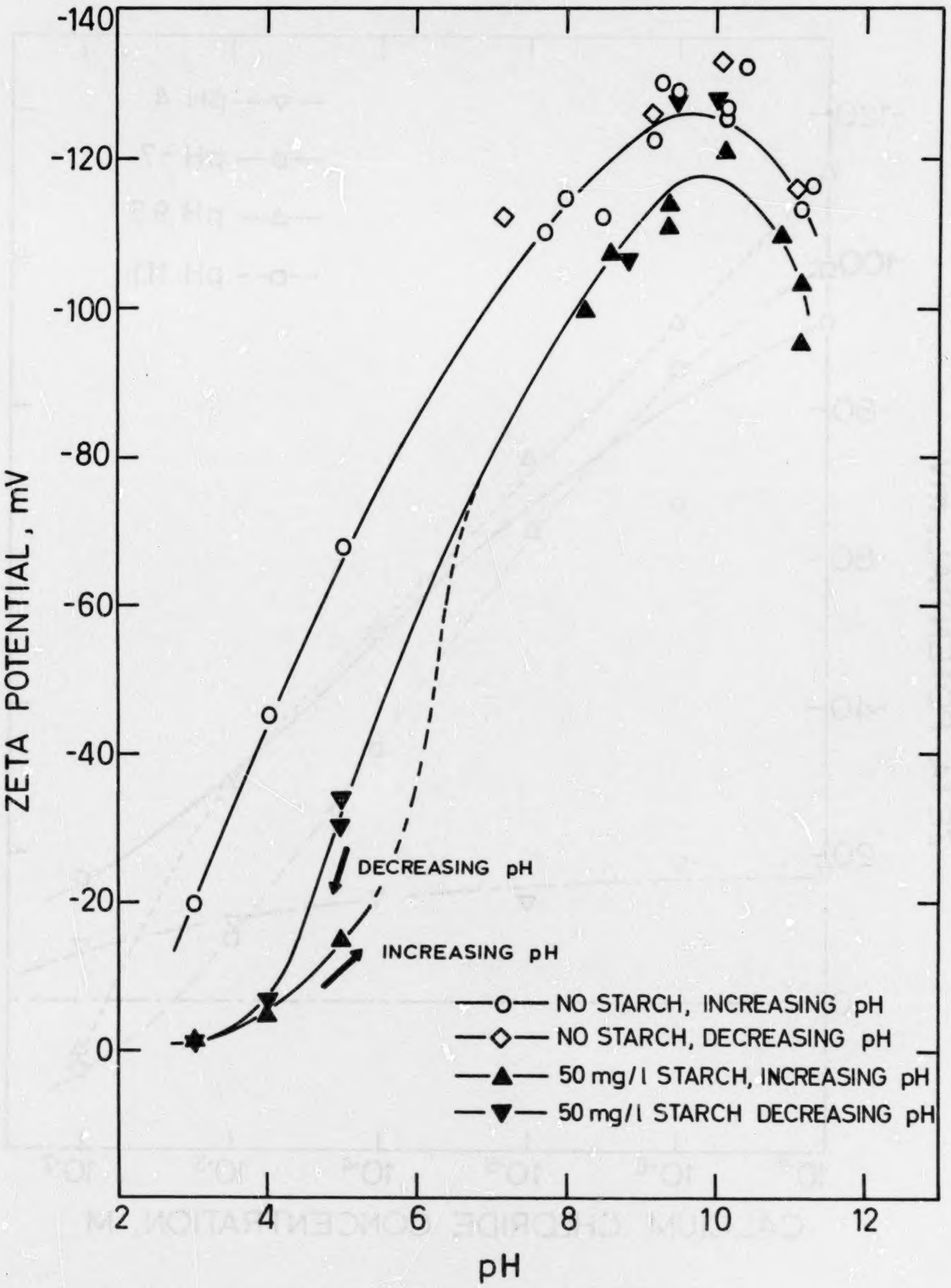


FIGURE 44. Zeta Potential of Quartz as a Function of pH in the Absence and in the Presence of 50 mg of Corn Starch per Liter

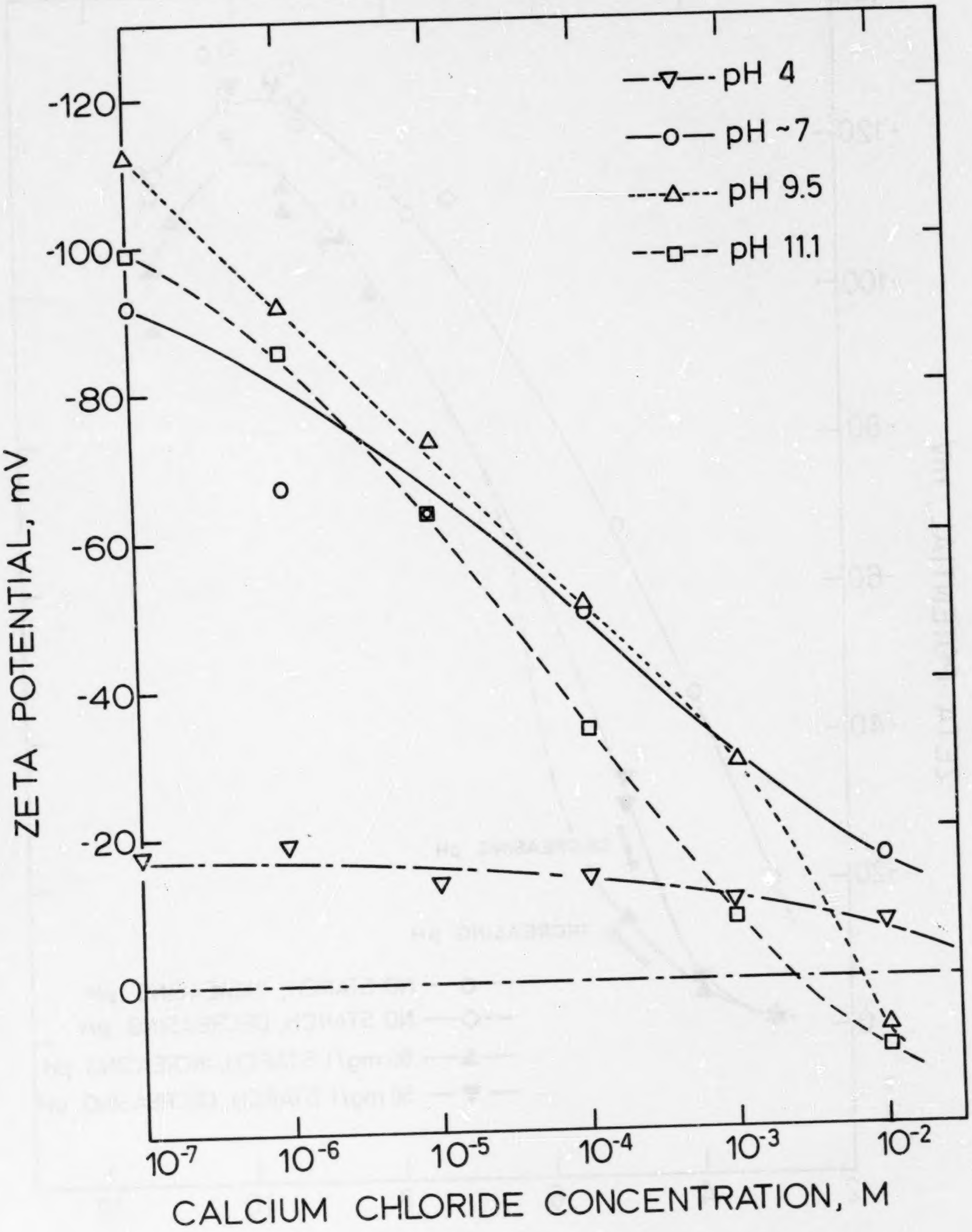


FIGURE 45. Zeta Potential of Brazilian Quartz as a Function of Calcium Chloride Concentration

presence of 50 mg of corn starch per liter, are presented in Figure 46. As evident, the zeta potential did not reverse its sign up to 10^{-2} M in all four cases, but their magnitude is affected appreciably. Due presumably to the stronger interaction with calcium ion at high pH, the quartz surface adsorbed a greater amount of corn starch, thereby approaching the zero zeta-potential line at lower concentrations of calcium chloride. Here again, strong interaction of the adsorbed calcium ion and starch adsorption is indicated. These observations are in line with the results of the flocculation tests given in Table 1 and Figure 10: that the most effective flocculation condition is obtained in highly alkaline solution at high calcium chloride concentrations.

Since the cationic starch was found to be quite effective in clarifying the quartz suspensions, cursory streaming-potential measurements were made on the Brazilian quartz using a 0.067 D.S. cationic starch. Three series of experiments were performed in which the solution pH was kept constant at 5.0, 9.5, and 11.2. The results are shown in Figure 47. It is readily apparent that the zeta potential changes its sign at very low concentrations of the cationic starch, and that the zeta-potential readings remain constant at higher concentrations, although the constant values are dependent on the pH. Since the saturation coverage by the cationic starch of quartz is known to increase with the solution pH,[15] the difference in the zeta potentials at the three pH values may be attributed to the difference in the adsorption densities. It becomes of much interest to test the effects of the degree of substitution of the cationic groups and of the cationic polyelectrolyte.

Viscosity Measurements

To investigate the effect of pH and calcium chloride concentration on viscosity, a stock starch solution was diluted and its pH was adjusted to a desired value so that a final concentration of 0.4 percent by weight was obtained. Hydrochloric acid and sodium hydroxide were used as pH regulators. The results of the relative viscosities as functions of pH are given in Figure 48(a). A sharp viscosity minimum is observed near pH 3.5, which may correspond to the isoelectric point of the solubilized starch.[28]

The effect of calcium chloride concentration on the relative viscosity was determined at pH 7 and 11, and the results are given in Figure 48(b). It is interesting to note that the relative viscosity at pH 7 remained more or less constant, regardless of the calcium chloride concentration. At pH 11, however, the relative viscosity decreased as the calcium chloride concentration was increased indicating that an interaction between the negatively-charged starch and the positively-charged calcium ion is more pronounced at high pH. This behavior, which is known as the electroviscous effect,[28] implies that the starch molecules become more tightly coiled as the calcium-ion concentration is increased.

The change in the conformation of starch molecules at a high concentration of calcium chloride may influence the flocculation behavior. To check

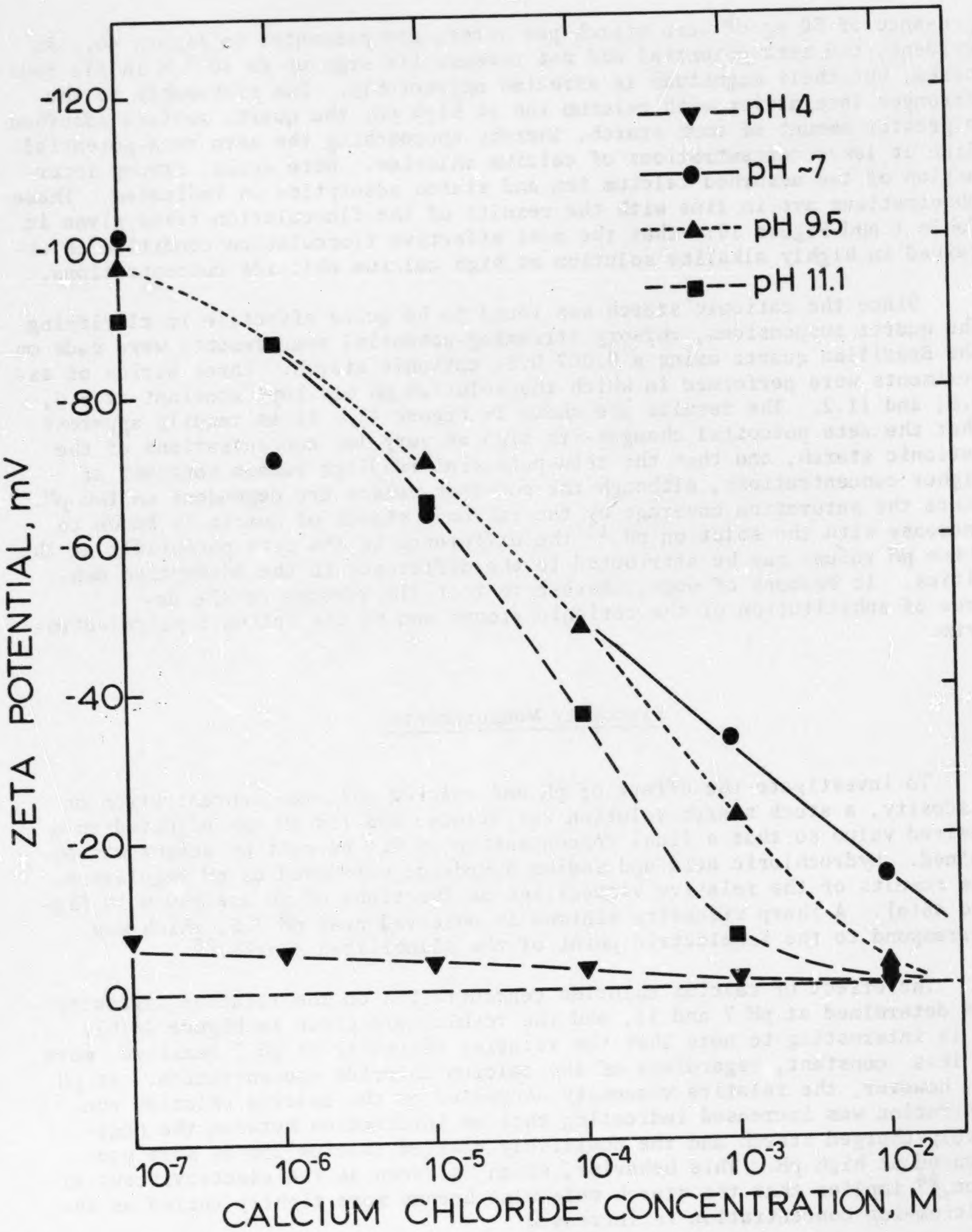


FIGURE 46. Zeta Potential of Brazilian Quartz as a Function of Calcium Chloride Concentration in the Presence of 50 mg/l Corn Starch

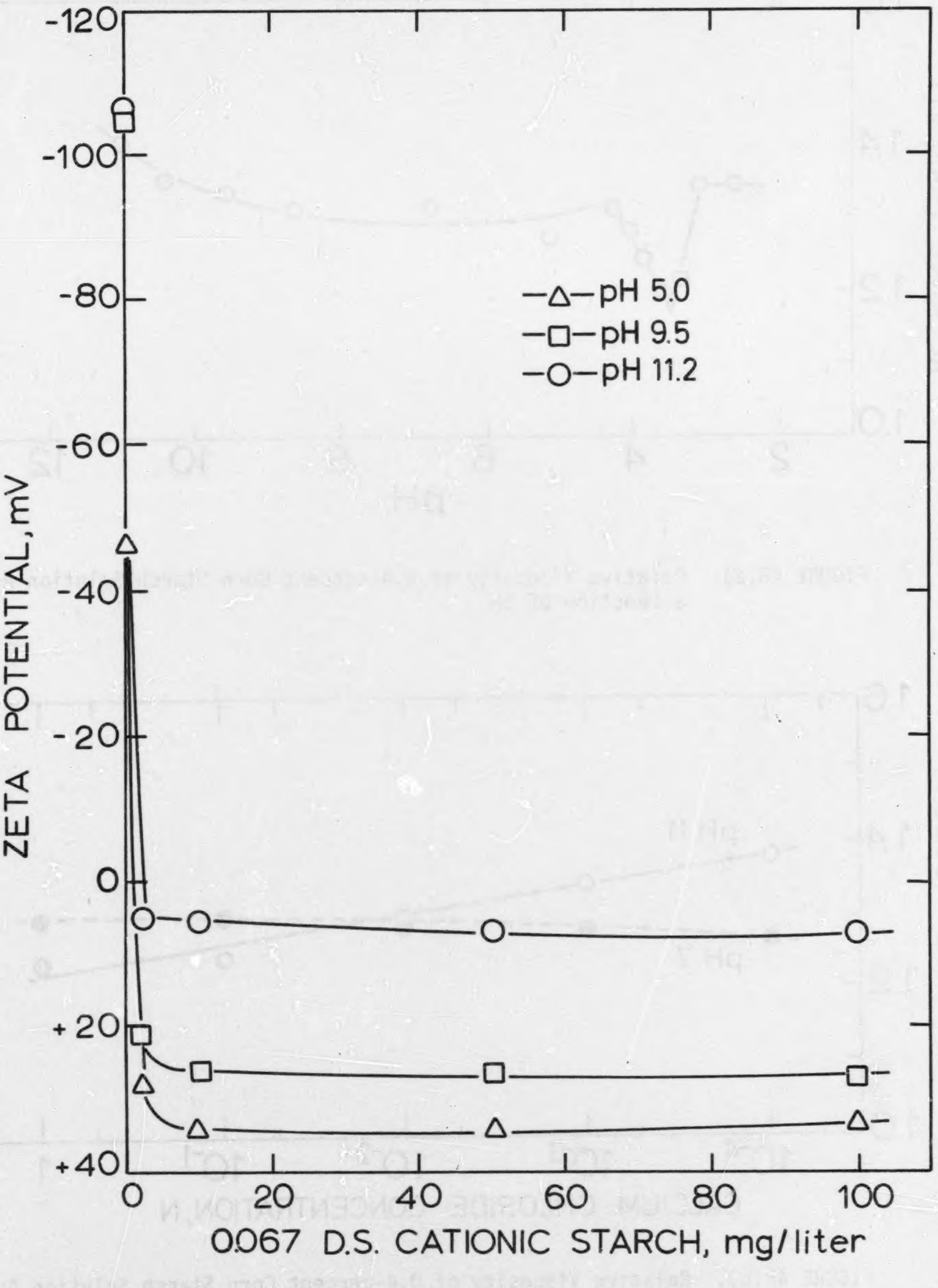


FIGURE 47. Zeta Potential of Brazilian Quartz as a Function of 0.067 D.S. Cationic Starch at pH 5.0, 9.5 and 11.2.

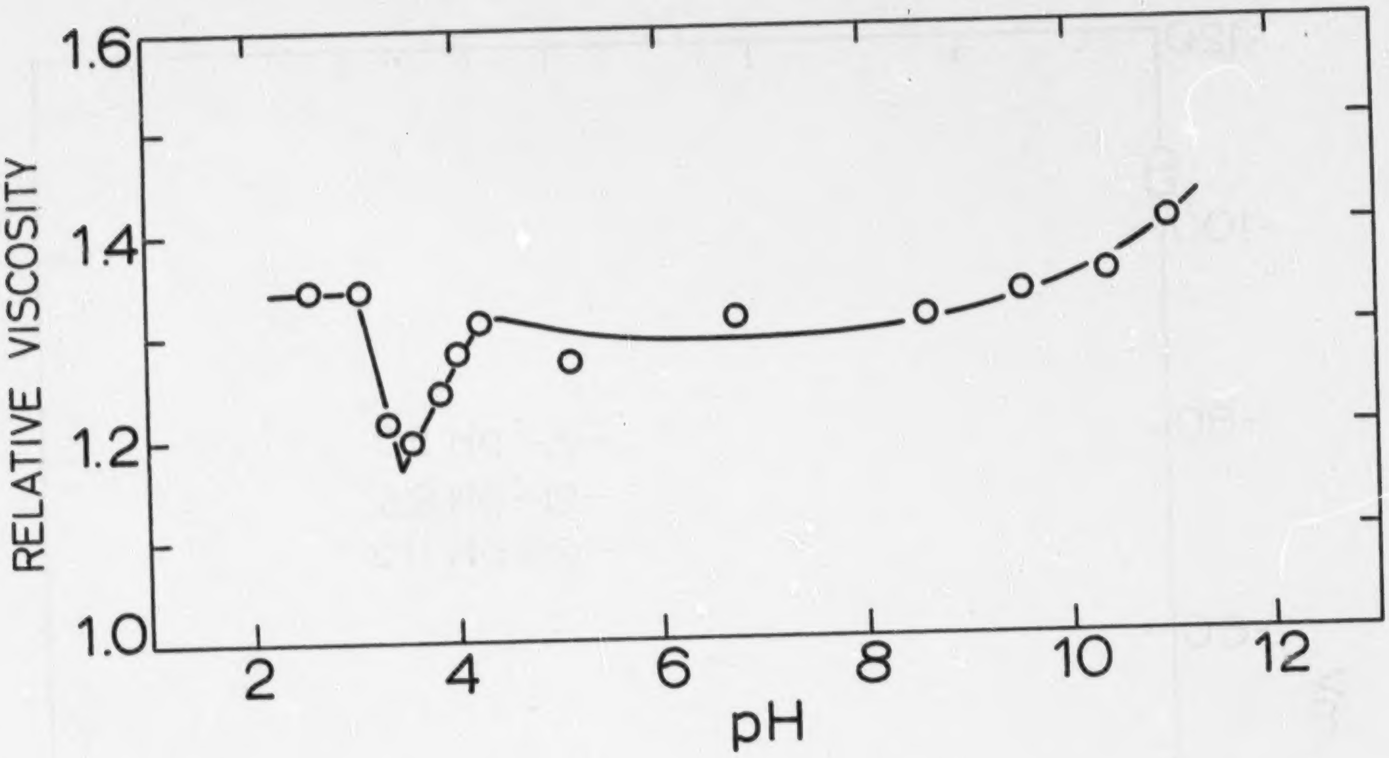


FIGURE 48(a). Relative Viscosity of 0.4-percent Corn Starch Solution As a Function of pH

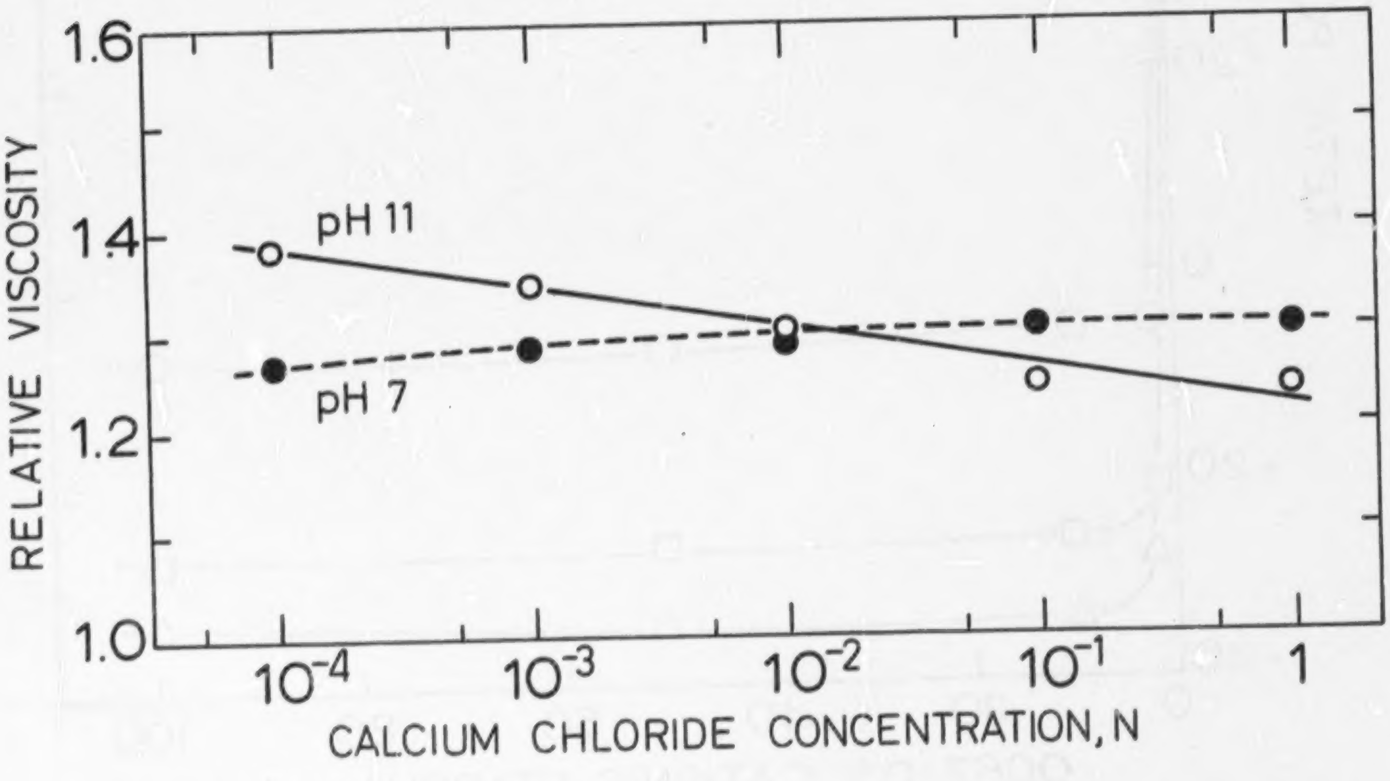


FIGURE 48(b). Relative Viscosity of 0.4-percent Corn Starch Solution As a Function of Calcium Chloride Concentration this particular point several series of flocculation tests were performed with quartz samples and with goethite samples. In each series the calcium chloride concentration was kept constant and the pulp pH was maintained either at natural near neutral pH, or at 11. The settling rates of quartz and goethite thus obtained as functions of the level of starch addition were plotted in Figures 49(a) and 50(a), respectively. As seen in these figures, the levels of the starch addition where the maximum settling rates were obtained varied widely with the calcium chloride concentration. The best comparison of the flocculation behavior then may be made by the maximum settling rates.

In Figure 49(b) the maximum settling rates for the quartz sample were plotted against the calcium chloride concentration. As seen in the figure, the settling rate at pH 7 decreased gradually with increasing calcium chloride concentration as expected. At pH 11, however, the settling rate increased markedly to 10^{-1} N calcium chloride. The increase up to this concentration may be attributed to the increased adsorption of starch accompanying the increased adsorption of calcium ions on the quartz. This point is reflected in the increased level of starch addition where the maximum settling rates are observed. The decrease in the maximum settling rate above a calcium chloride concentration of 10^{-1}N must then be caused by the change in the conformation of the starch. The somewhat lower level of starch addition where the maximum is observed might also suggest some change in the charge characteristics of the starch molecules themselves. It certainly becomes of interest to study the zeta potential of starch under similar conditions using the moving boundary method.

For the goethite sample the maximum settling rates both at pH 7 and 11 are seen in Figure 50(b) to decrease gradually with increasing calcium chloride concentration. Since the goethite surface is less negative than the quartz surface, the effect of calcium ion on the adsorption of starch is expected to be less, and the decrease as shown must then reflect the effect of the conformation of starch more or less directly. The maximum settling rate at pH 11 in the presence of 10^{-1}N calcium chloride, however, appears to be somewhat higher than the curve drawn through the points. This might indicate a similar effect of calcium ion as observed for the quartz sample at pH 11, but to a much less extent. The results of streaming-potential measurements on the goethite sample show that the sign of the zeta potential may be reversed at pH 11 when the calcium chloride concentration exceeds 4×10^{-4} M (Figure 40).

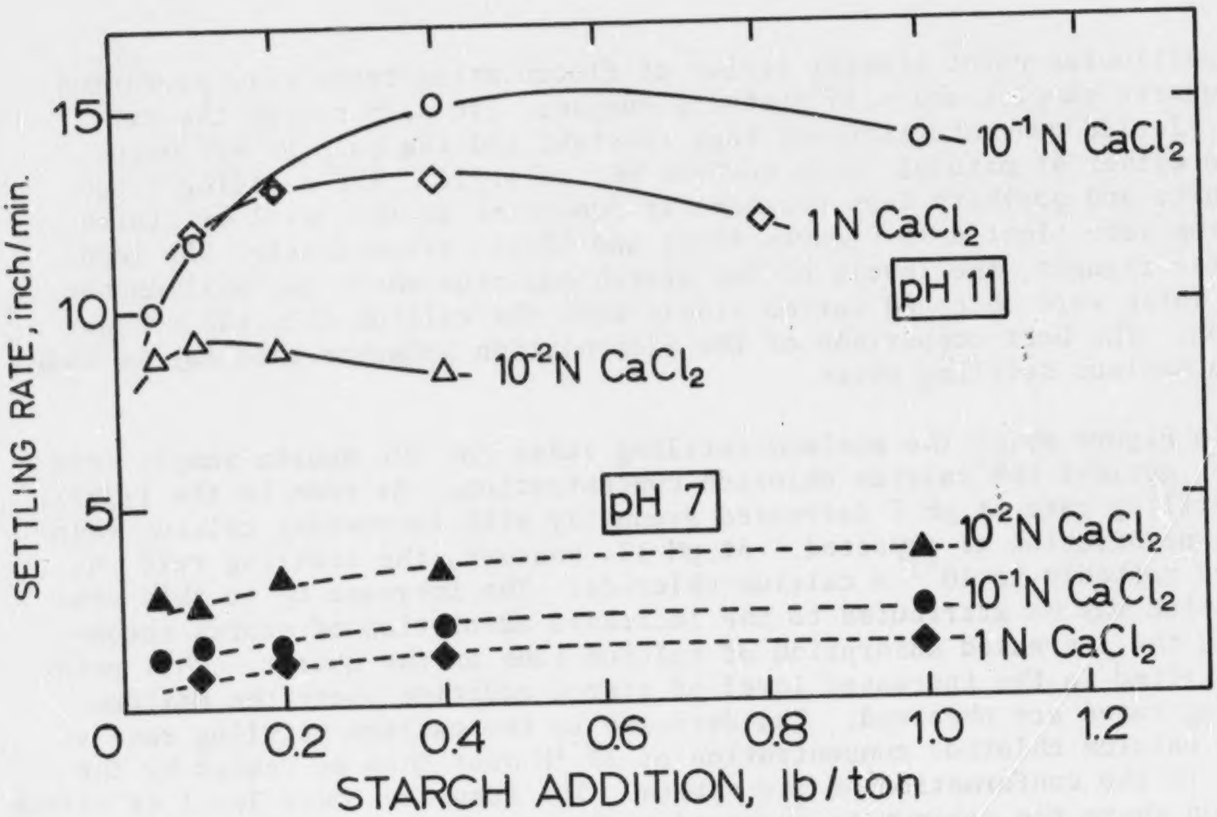


FIGURE 49(a). Flocculation Test Results on Quartz as a Function of Starch Addition at Different Concentrations of Calcium Chloride at pH 7 (Lower Curves) and pH 11 (Upper Curves)

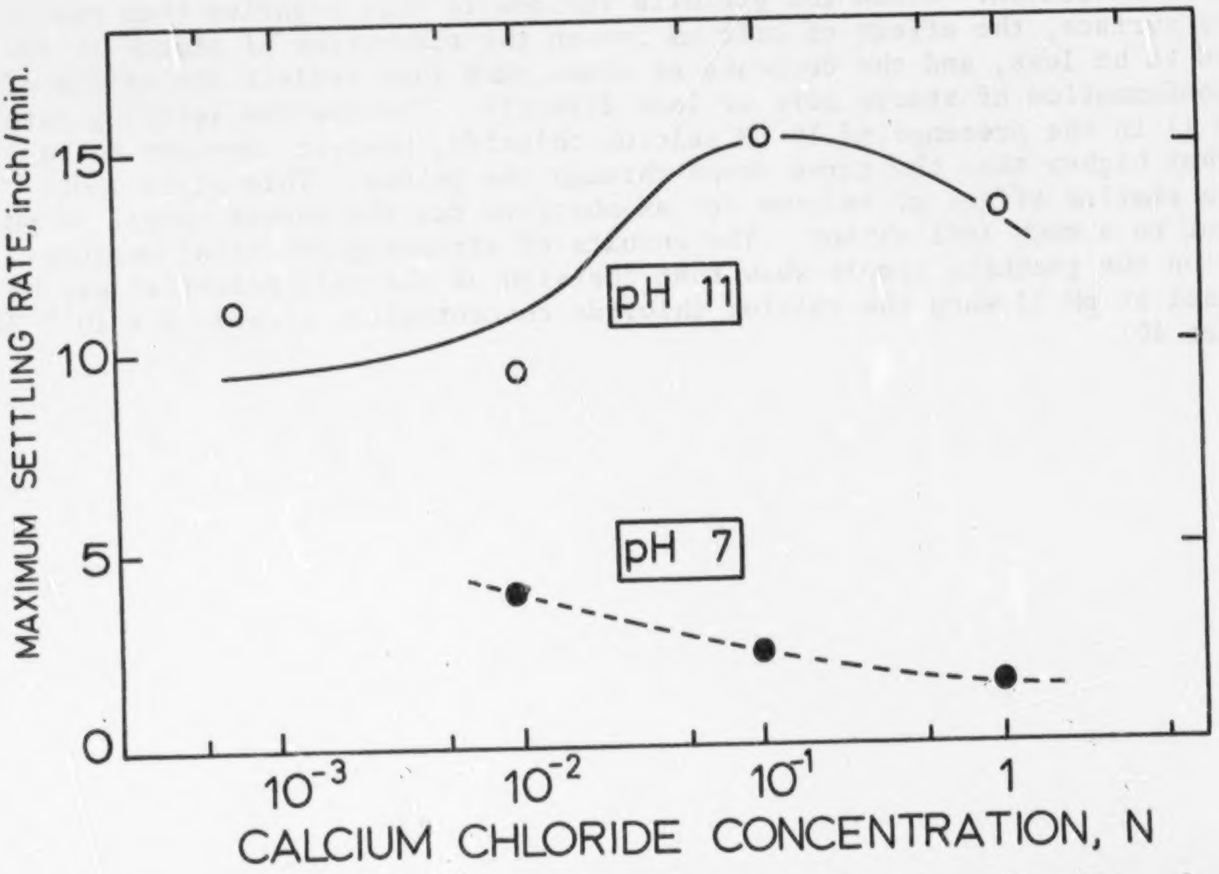


FIGURE 49(b). Maximum Settling Rate of Quartz as a Function of Calcium Chloride Concentration

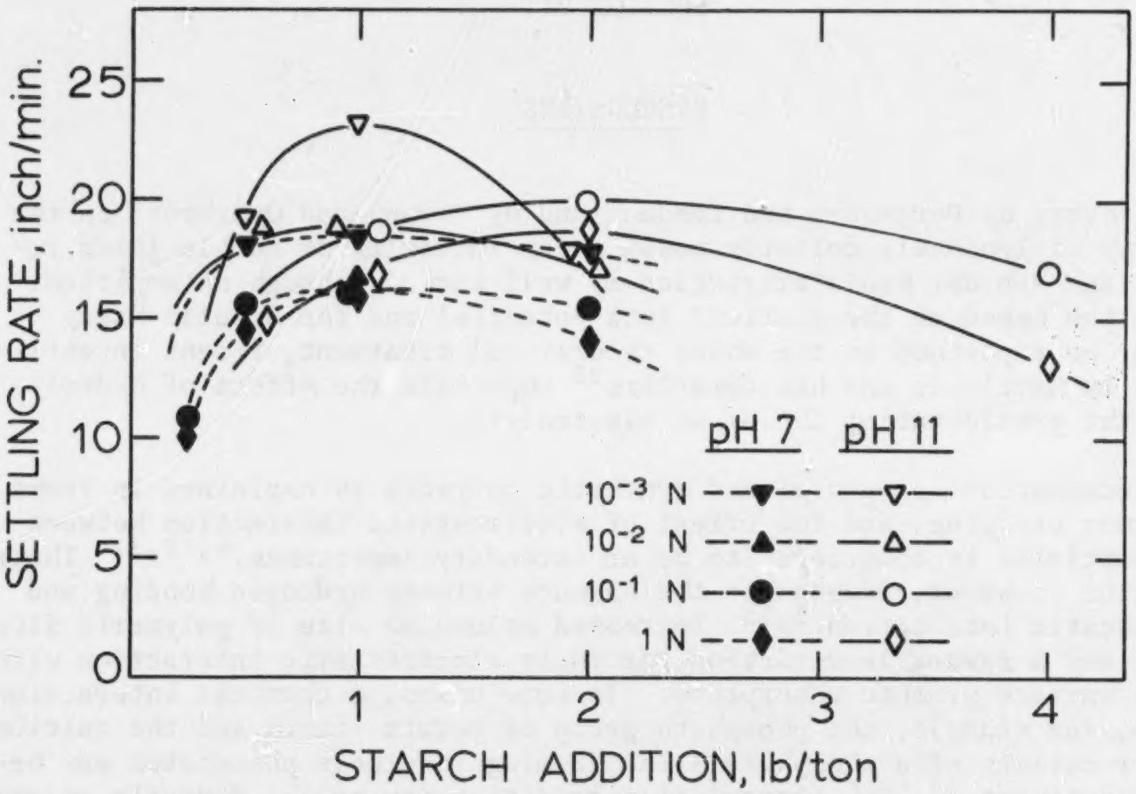


FIGURE 50(a). Flocculation Test Results on Goethite as a Function of Starch Addition at Different Concentrations of Calcium Chloride at pH 7 and 11

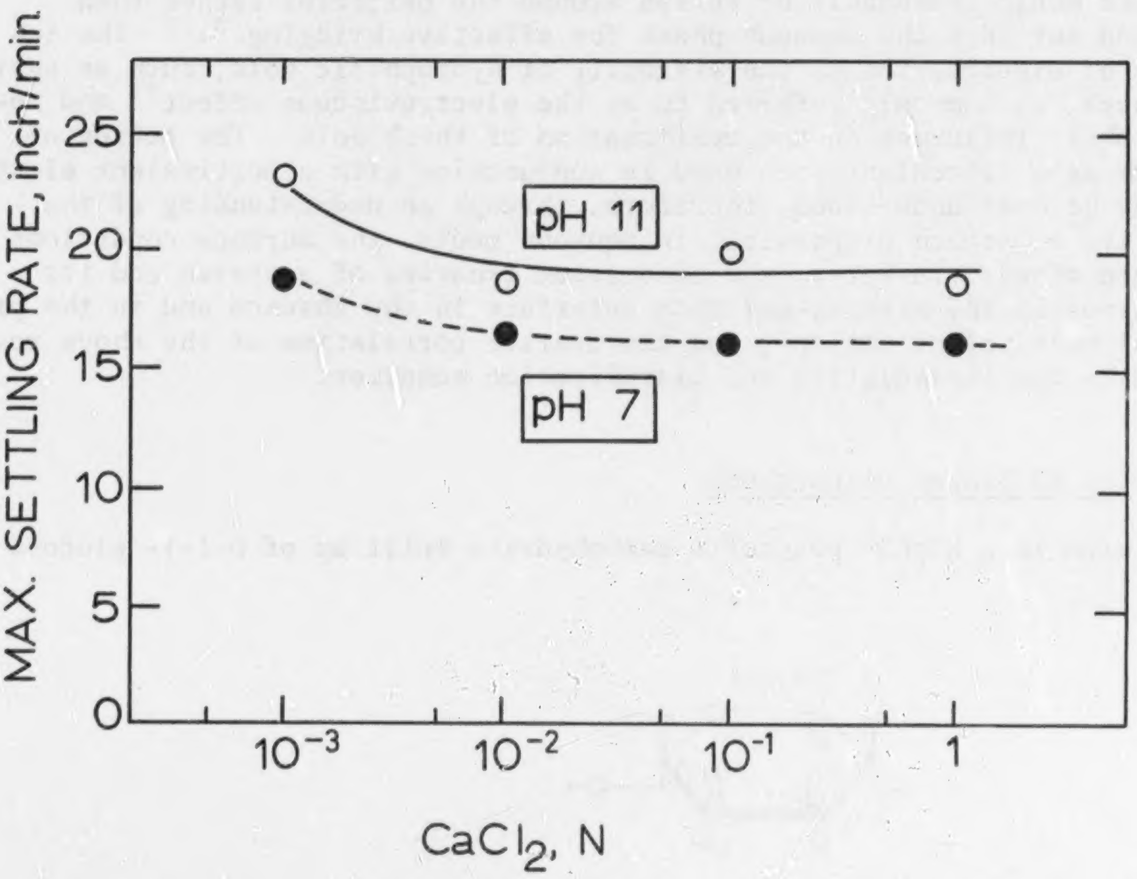


FIGURE 50(b). Maximum Settling Rate of Goethite as a Function of Calcium Chloride Concentration

SECTION VII

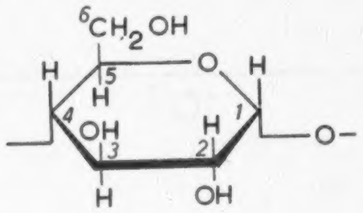
DISCUSSIONS

A theory by Derjaguin and Landau, and by Verwey and Overbeek[5] on the stability of lyophobic colloids based on an interplay of double layer repulsion and van der Waals' attraction is well known. Though an empirical formulation based on the critical zeta potential and the Schulze-Hardy rule may be explained by the above theoretical treatment, recent investigations by Matijevic and his coworkers[29] emphasize the effect of hydrolysis of the precipitating ion of an electrolyte.

Flocculation by natural and synthetic polymers is explained in terms of polymer bridging, and the effect of electrostatic interaction between solid particles is considered to be of secondary importance.[4,30,31] Their adsorption, however, depends on the balance between hydrogen bonding and electrostatic interaction.[3,15] Increased molecular size of polymeric flocculants and a favorable condition for their electrostatic interaction with mineral surface promote adsorption. In some cases, a chemical interaction between, for example, the phosphate group of potato starch and the calcium or other cations of a phosphate slime forming insoluble phosphates may become predominant.[32] The flocculation condition may not be directly related to the adsorption densities since the bridging depends on the conformation of the polymer chain at the interface.[4,9] The role the conformation of a polymer plays at the interface is clearly indicated by the detrimental effect of an excessive agitation on a suspension. Here, the adsorbed polymer chain would presumably be coiled around the particles rather than stretched out into the aqueous phase for effective bridging.[3,33] The influence of electrolytes on the viscosity of hydrophilic sols, such as agar and starch, is commonly referred to as the electroviscous effect[28] and reflects their influence on the conformation of these sols. The action of a starch as a flocculant when used in conjunction with a multivalent electrolyte may be best understood, therefore, through an understanding of the properties of starch dispersions in aqueous media, the surface conditions of a pure mineral in water, the adsorption behavior of a starch and its derivatives at the mineral-solution interface in the absence and in the presence of multivalent cations, and the overall correlation of the above results with the flocculation and clarification behavior.

Properties of Starch Dispersions

Starch is a highly polymeric carbohydrate built up of D-(+)- glucose units



and its molecular weight ranges from 50,000 up to several millions. Corn starch consists of two types of polymers: a linear amylose composed of 200 to 1,000 pyranose rings bonded together through oxygen atoms in positions 1 and 4, and a branched amylopectin with 1,500 or more pyranose rings connected with periodic branching at positions 1 and 6. The proportions of each are reported to be 25 percent amylose and 75 percent amylopectin.[34] In chemically modified starches the substituent groups, $-O-CH_2COO^-Na^+$ and $-O-CH_2-CHOH-CH_2N(CH_3)_3^+Cl^-$, have been introduced in varying amounts mainly at positions 2 and 6 to the extent indicated by the degree of substitution. The maximum degree of substitution attainable is 3.0 including the OH- group at position 3.

The structure of starch molecules in aqueous solutions is complicated by their association through hydrogen bonding. The infrared spectra of starch indicate that the hydroxyl groups are strongly hydrogen bonded.[35] The location of the hydrogen bonding in the starch molecules depends largely on the spatial configuration involving the hydroxyl groups in the pyranose ring. The hydroxyl groups at carbon atom No. 6 form perhaps the strongest O-H .... O bonds, whereas the other hydroxyl groups at carbon atoms No. 2 and 3 are generally more occluded than the protruding hydroxyls at carbon atom No. 6, especially in the linear starch molecules. The branched chain aggregates of starch form relatively stable starch-water complexes due to the availability (for spatial reasons) of some more hydroxyl groups at carbon atoms No. 2 and 3.[36]

An unmodified corn starch is negatively charged due presumably to the presence of a small amount of fatty acid, esterified with the carbohydrate.[37] Ionization of the hydroxyl groups, particularly at positions 2 and 6 of the glucose unit, is also thought to contribute towards the development of a charge on the starch.[38] In the electrophoretic mobility measurements on the granules of unmodified corn starch[15] the sign of the electrical charge remained negative in the pH range from 3 to 11 indicating that the isoelectric point was not reached, although the electrophoretic mobility decreased at higher and lower pH values due presumably to the compression of the electrical double layer around the starch granules. The viscosity of a starch dispersion, as shown in Figure 48,undergoes a minimum point near pH 3.5, which may correspond to the isoelectric point.[28] However, a cursory measurement indicated that in the presence of corn starch the streaming potential of quartz remains negative in this pH region. Since the adsorption density of starch is not too high, the zeta potential may be more strongly influenced by the negatively charged quartz surface. It becomes of interest to study the zeta-potential of a solubilized starch in more detail using the moving-boundary technique. The isoelectric point of potato starch is reported to be at 4.6.[39]

The electrophoretic mobility measurements also determined that the cationically and anionically modified starches used in the present investigation were respectively positively and negatively charged, and that there were no changes in the sign of electrical charge in the pH range from 3 to 11.[15] Evidently, these functional groups remain ionized over the stated pH range.

Viscosity measurements provide a most convenient method of determining relative molecular sizes of starch in solutions.[23] Both mechanical shearing and prolonged heating are reported to decrease viscosity markedly, and, therefore, the average molecular weight, and also a starch solution left standing in a flask lowers its viscosity over a period of a few days probably through biological degradation.[6] The standardization of the preparation procedure becomes imperative for the starch solution in order to have consistent molecular weight throughout the test program. For a given starch solution the change in viscosity reflects the change in the conformation of the starch molecules. An increase in viscosity with increasing pH (Figure 48) would indicate the ionization of the hydroxyl groups, thereby the starch structure resulting in more stretched-out conformation. The presence of an excess concentration of calcium ion neutralizes the negative charge on the starch structure and makes the starch molecules to coil more tightly. The effect of calcium ion on the viscosity of corn starch is noted to be more pronounced at pH 11 than at pH 7, a phenomenon parelleling the action of calcium ion on quartz.

Surface Conditions of Quartz and Goethite in Water

In developing a theory of the stability of lyophobic colloids Verwey and Overbeek[22] differentiated between the adsorption behaviors of ions in solution on a given solid surface and classified them into three groups, namely, potential-determining ions, indifferent ions, and specifically-adsorbed ions. Those ions which establish equilibrium at the interface and which determine the potential drop between the solid and the liquid phases are termed potential-determining ions and are responsible for the electrical charge observed on the solid surface.

For oxide minerals, it is postulated[40] that the oxygen ions in the surface undergo the following reaction:

$$O^{=}_{(\text{surface})} + H_2O \rightleftharpoons 2OH^{-}\ (\text{solution})$$

It follows that hydroxyl ions (and, accordingly, hydrogen ions) are involved in the electrolytic reaction at the interface and are thought to be the potential-determining ions. Streaming-potential measurements on a number of oxides as a function of pH and in the presence of different concentrations of an indifferent electrolyte substantiated this.[41,42] An increase in pH drives the reaction to the left and increases the concentration of oxygen ions at the surface, thereby making the surface more negative. Conversely, a decrease in the pH should cause the reaction to go to the right and the surface oxygen-ion concentration decreases. At a certain pH, the surface becomes electrically uncharged, and is referred to as the isoelectric point. In a solution with a pH below this value the surface becomes positively charged. The isoelectric points of the goethite and the Brazilian quartz samples are seen in Figures 39 and 44 to be at pH 6.7 and near pH 2, respectively. These values are in good agreement with those reported previously.[13,40] Schematic illustrations of the origin of electrical charge on silica[26] and hematite[43] based on this concept, are given in the literature.

The Schulze-Hardy rule relates the power of active ions coagulating sols with the valence of the ions. In its original form the valence of active ions was taken directly. Matijevic[29] emphasized the importance of the hydrolyzed species of metal ions in effecting the reversal of charge on lyophobic colloids. In line with his view streaming-potential measurements on quartz as a function of calcium chloride concentration (Figure 45) showed that the zeta potentials remained negative irrespective of calcium chloride concentration at pH 4 and near 7. At pH 9.5 and 11, however, the sign of the zeta potential on the quartz was reversed at calcium chloride concentrations of 10^{-2} M and 2.5×10^{-3} M, respectively, suggesting that $CaOH^+$ might be the effective form for adsorption. In fact, Clark and Cooke[49] arrived at the same conclusion by comparing the equilibrium concentrations of the different species of calcium ion with the adsorption data in connection with the anionic flotation of this mineral. The reversal of the sign of the zeta potentials was also noted on goethite at pH 10.7 (Figure 40). This observation is of particular interest in the anionic silica flotation of iron ores, since the ability of calcium ion to reverse the zeta potential of goethite in the highly alkaline pH range might activate this mineral along with quartz for possible flotation with an anionic collector.[50] This clearly indicates the need of a starch depressant in such a system.

In the discussions to follow it will be shown that the adsorption of a starch flocculant is governed by the electrical interaction between the starch and the charged mineral-solution interface. For the negatively charged corn starch to be effective the mineral surface must be positively charged. It then becomes of interest to investigate the effects of magnesium ion which is known to form $MgOH^+$ at a much lower pH,[49] of aluminum ion which forms polymeric hydrous oxide ion $[Al_8(OH)_{20}]^{+4}$ at near neutral pH,[51] and of ferric ion which forms hydroxlyzed iron (III) polymers.[27]

Adsorption Mechanism of Starches

In the flocculation of mineral suspensions by natural and synthetic polymers, not only the adsorption density of the polymers, but also the manner by which the polymers are adsorbed at the interface becomes important. Several different approaches have been proposed for a theoretical treatment of polymer adsorption.[44,45] These theories appear to differ primarily in their depictions of the method by which the polymers are secured at the interface, but it is generally accepted that a polymer molecule is attached with short sequences of segments on the surface and that the unattached segments extend into the solution as loops. The relative number and arrangement of the attached and unattached segments define the conformation of the adsorbed molecule.

No single theoretical treatment has been shown to cover the whole picture even with polymers of well-defined composition and molecular weight. The distribution of the molecular weight of starches prepared in the manner described in the present investigation was necessarily undefined and, therefore, precluded the theoretical analysis based on these theoretical treatments. Nevertheless, the adsorption isotherms of corn starch and a cationic starch on quartz and hematite,[15] shown in Figures 51(a) and (b), are seen to follow the general shape of the Simha-Frisch-Eirich plot.[45]

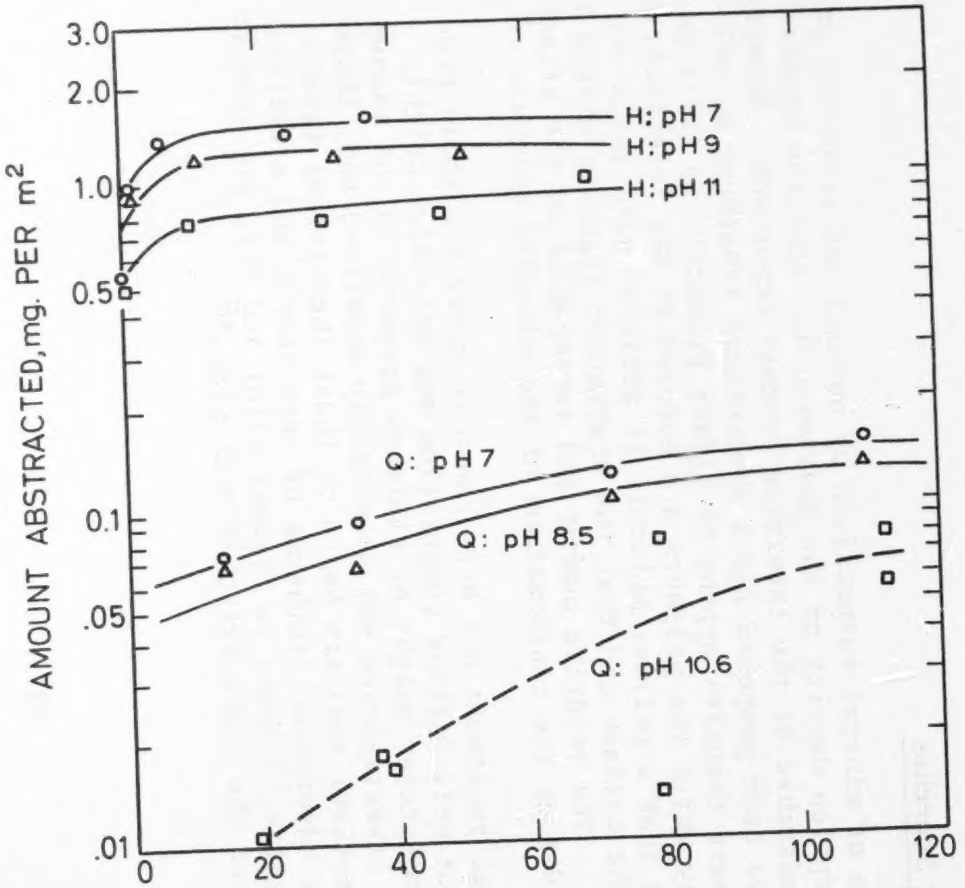


FIGURE 51(a). Adsorption of Corn Starch on Hematite (H) and Quartz (Q)[15]

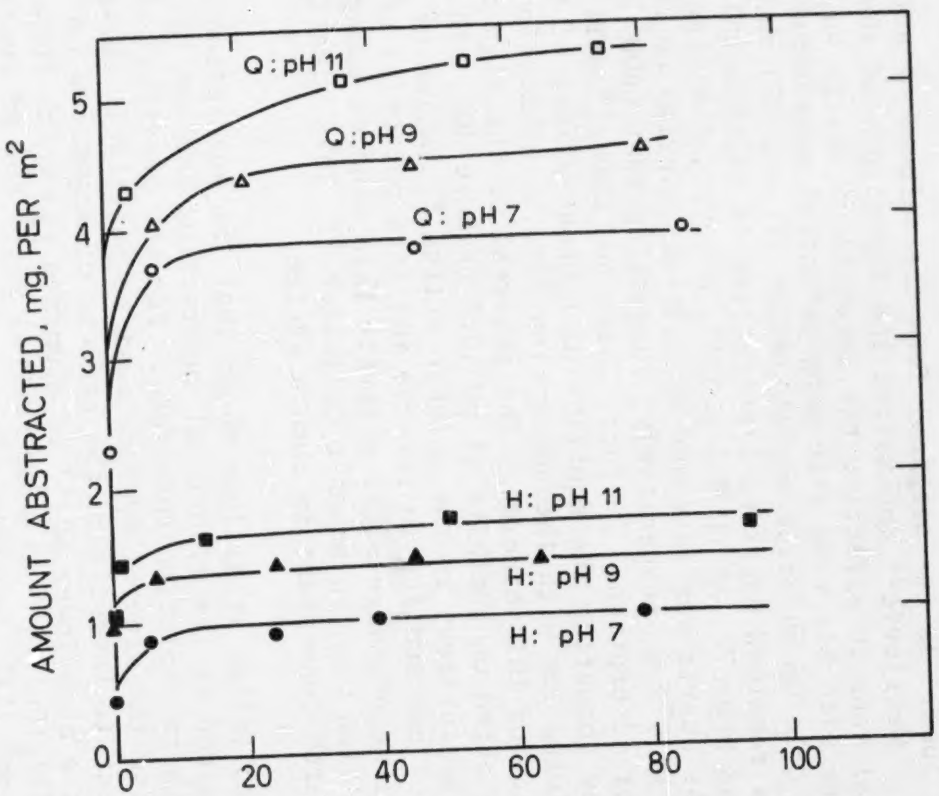


FIGURE 51(b). Adsorption of Cationic Starch on Hematite (H) and Quartz (Q)[15]

In Figure 51 it is readily apparent that corn starch is more strongly adsorbed on hematite than it is on quartz, but the adsorption densities of the cationic starch are higher on quartz than on hematite. If a closer examination of the individual isotherms is made, it will be noted that the adsorption of the corn starch decreases with increasing pH, whereas that of the cationic starch increases with increasing pH both on quartz and on hematite. Quartz is more electronegative than hematite in aqueous suspensions in the pH range 7 to 11 since the isoelectric points of quartz and hematite suspensions exist at a pH near 2 and 6.7, respectively, and corn starch is negatively charged in aqueous solutions in the same pH range. The diametrically-opposite adsorption behavior of the corn starch and the cationic starch on these two oxide minerals may be understood if an electrostatic interaction exists between the starch and the mineral surface. The electrostatic repulsive forces acting between the oxide mineral surface and the corn starch molecules serve to hinder adsorption. It is obvious then that the adsorption is caused by some nonionic process.

The hydrogen bonding between hydrogen in starches (COOH, OH, NH, etc.) and oxygen on the oxide mineral surface is generally accepted as being responsible for their adsorption, similar to the adsorption of polyelectrolytes postulated by Michaels.[46] Evidence of hydrogen bonding in the adsorption of polyacrylamide on silica was found by infrared spectroscopy.[47] Although the hydrogen bond is relatively weak, since thousands of bonds are formed per polymer molecule, the total bonding energy per polymer molecule becomes very large.[31] The adsorption of starches has been schematically viewed, as shown in Figure 52, by a model incorporating the electrostatic and hydrogen-bonding phenomena.[15] The adsorption by hydrogen bonding is considered to be the same for cationic, unmodified corn, and anionic starches, assuming that the molecular weights are the same for all three starches. Because of the combined effect of electrostatic attraction and the hydrogen-bonding forces, the adsorption of the cationic starch by quartz and hematite is quite high. The adsorption of unmodified corn starch, being negatively charged, and in particular, of an anionic starch will be lowered because of electrostatic repulsion. The so-called "squeezing-out" effect, postulated for the adsorption of relatively large-sized anions, such as NO_3^- and ClO_4^-, at a mercury-solution interface,[48] may also have to be taken into consideration for the adsorption of large starch molecules at a solid-solution interface.

A strong affinity of corn starch toward hematite is indicated in Figure 51 in the steep rise in the adsorption density at low concentration; the isotherms then reach a saturation coverage corresponding to a particular pH. The adsorption isotherm on hematite and the zeta-potential curve on goethite in the presence of corn starch (Figure 38) show strikingly similar trends. The constant values of zeta potentials in the high concentration range of starch may reflect the saturation coverage observed in the adsorption isotherms. The irreversibility of the adsorption of corn starch, shown by the hysteresis of zeta potentials as a function of pH on goethite (Figure 39) and possiby on quartz at low pH (Figure 44), affords additional evidence that corn starch is strongly adsorbed on uncharged goethite via hydrogen bonding.

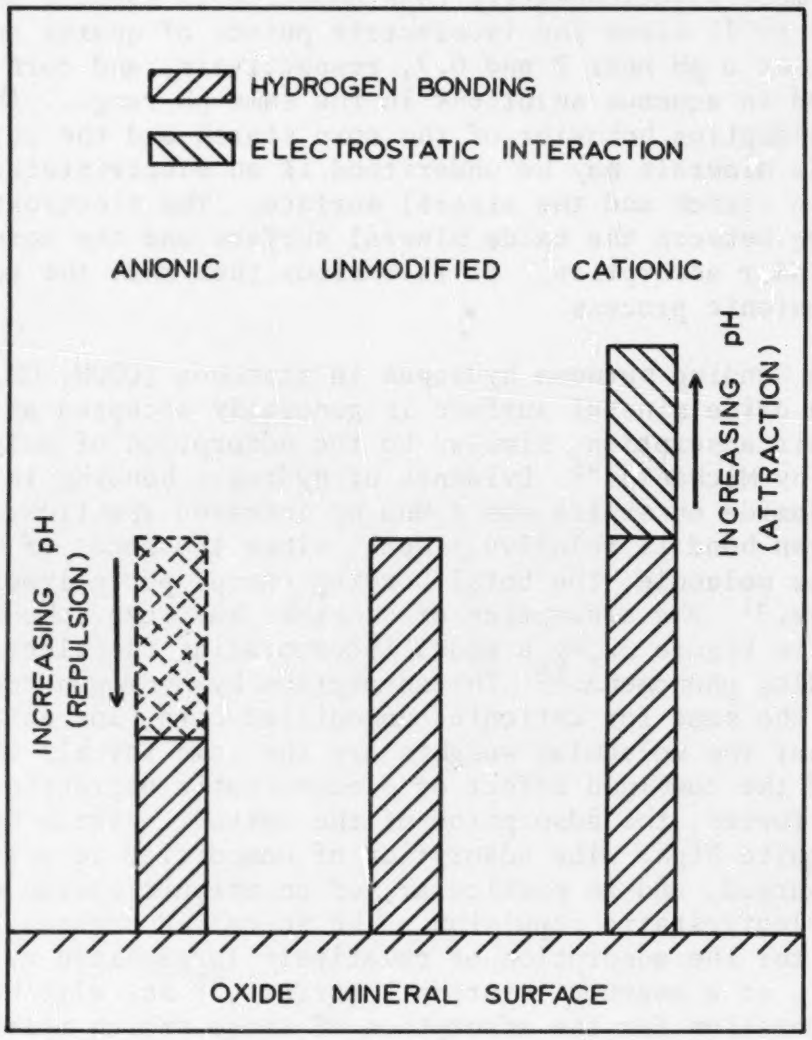

HYDROGEN BONDING
ELECTROSTATIC INTERACTION
ANIONIC
UNMODIFIED
CATIONIC
INCREASING pH
(REPULSION)
INCREASING pH
(ATTRACTION)
OXIDE MINERAL SURFACE

FIGURE 52 A Model Showing Mode of Adsorption by Various Starches on Oxide Mineral Surfaces.[15]

In the present discussion the adsorption behaviors of starches on hematite and goethite are mentioned, more or less, interchangeably. Since the isoelectric points of both hematite and goethite are located at the same pH of 6.7, and since their flotation behaviors have been shown to be nearly identical,[52] the surface properties of these two minerals may be regarded as behaving in a similar manner. Goethite was chosen for the streaming-potential measurements because difficulty was encountered during the experiment with hematite in the determination of the zeta potential due presumably to the surface conductance.[53] Measurements of the surface area of goethite by the krypton adsorption method, however, became somewhat superfluous for expressing the adsorption density of giant polymer molecules, such as starch and polyacrylamide, due to the extremely porous structure of goethite. In fact, it was reported that the surface area of goethite determined by the nitrogen adsorption method was virtually independent of the fineness of the grind.[54]

The number of hydrogen-bonding groups in a starch molecule and possibly the squeezing-out effect of the starch molecule will be dependent on the molecular size. The adsorption density would then be expected to decrease with the molecular size. The homogenization of a starch dispersion and the pyrolytic degradation of a corn starch into a British gum reduce the average molecular size, which may be attested by the viscosity measurements. As a result, the abstraction of homogenized corn starch and of British gum by quartz and hematite was reported to be appreciably lower.[6,15]

The presence of calcium ions in solution enhances the adsorption of corn starch both on quartz and on hematite appreciably.[6] This phenomenon is shown in the response contours of starch abstraction by quartz in Figure 10(c). According to the present interpretation based on the electrical interaction between the charged mineral surface and the starch, the effect of calcium ions is obviously to lower the zeta potential of negatively charged minerals, thereby the electrostatic repulsion, as illustrated schematically in Figure 52, is reduced. When the zeta potentials of quartz as functions of calcium chloride concentration in the absence (Figure 45) and in the presence of starch (Figure 46) are compared, the most pronounced effect of starch is seen where the sign of the zeta potential of quartz reverses at high concentration of calcium chloride and at high pH. This was the condition where the most effective flocculation of quartz was shown to occur in Figure 10. Presumably the reversal of the sign of the surface charge due to adsorbed calcium ion promoted the adsorption of the starch for flocculation.

In addition, the interaction of calcium ions with starch molecules in solution should not be overlooked. With an increasing calcium chloride concentration, the starch molecules become more tightly coiled, as evidenced by the decrease in viscosity (Figure 48). It follows, therefore, that the presence of calcium ions in solution influences the adsorption behavior of starch not only by increasing its adsorption density but also by altering the conformation of the starch molecules at the interface. The interaction of starch molecules with calcium ions either in solution or at the surface of a mineral may also involve some chemical bond formation with a minor quantity of fatty acid inherently present in the starch structure.[38]

Flocculation Mechanism with Starches

In the flocculation of mineral suspensions with a polymeric reagent, natural or synthetic, two separate processes may be identified, namely, the adsorption of the polymeric flocculant and the formation of flocs.[4] The adsorption of a sufficient quantity of the flocculant appears to be a necessary condition, but it does not always lead to an effective flocculation of mineral suspensions. A unique geometrical arrangement, or conformation, of the polymeric molecules at the mineral surfaces is needed for successful bridging in the formation of large and stable flocs. Almost invariably an optimum dosage level exists for a given polymeric flocculant, and an excess of the flocculant tends to redisperse the flocs. A number of examples may be seen in the experimental results with both starches and polyacrylamides in Figures 11, 12, 15, 19, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, and 35. This is attributed to an increased hydration of the mineral surface due to an excessive adsorption of a hydrophilic colloid. The phenomenon is referred to as protection.[28]

The optimum level and the effectiveness of floc formation depend on a number of factors: the type, the mesh-of-grind, and the concentration of the minerals; the type , the functional group, and the molecular weight of the polymeric flocculants; the pH of the suspension; the type of and concentration of the electrolytes in solution; and the temperature of the suspension. For a suspension of a mineral, in particular a mixture of minerals, the proper selection and use of a flocculant would, therefore, be an exceedingly complex subject.

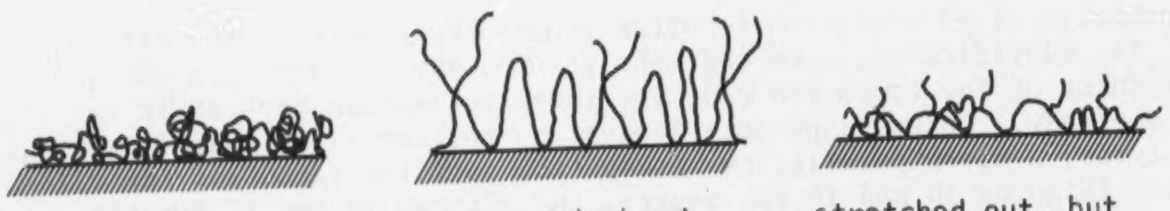
In Figures 11, 14, and 15, it is apparent that the maximum settling rate and clarity of the supernatant solution are obtained both on quartz and goethite suspensions at a point where an excess of starch begins to appear in the supernatant solution. The adsorption isotherms given in Figure 18 indicate that the maximum settling rate is observed when near saturation coverage for this particular experimental condition is attained. The critical levels of starch for quartz and goethite, however, differ nearly ten-fold. The importance of the adsorption density in flocculation is indicated by an observation that the maximum settling rate for goethite is three times greater than that for quartz. In the absence of calcium ions corn starch does not flocculate quartz due evidently to an insufficient adsorption. Here, both quartz and corn starch are negatively charged. In the presence of calcium ions the settling rate of a quartz suspension improves as the pH is raised (Figure 12). A strong interaction of calcium ions with quartz in highly alkaline solutions was indicated in the adsorption studies[49] and in the streaming potential measurements (Figure 45). Though the electrical charge on the mineral surfaces may be made more favorable for the adsorption of the negatively charged starch molecules, the effect of calcium ions on the conformation of the starch molecules (Figure 48) should not be overlooked. In addition, the electrical charge on the starch molecules may also be affected. The decrease in the maximum settling rate of quartz and of goethite with an increase in the calcium chloride concentration (Figures 49 and 50) affords evidence that the conformation at the interface is important. The increase in the maximum settling rate up to 10^{-1}N at pH 11 must presumably be due to an increased adsorption of starch resulting from the increased adsorption of calcium ion. Obviously, further experimental evidence is needed to confirm this particular point.

The mechanism of flocculation is often studied by examining the settling rate, the clarification, the sediment volume, the refiltration rate, and the thickness of the compacted bed, but these parameters may not be interrelated directly. Polymers produce larger and tougher flocs than do simple electrolytes; a close parallelism between the settling rates and the filtration rates (Figures 10 and 16 for quartz, and Figures 14 and 17 for goethite) reflects such a flocculation behavior. In fact, Smellie and LaMer[55] attempted to describe the flocculation behavior quantitatively from the refiltration rates, although their approach has recently been discredited.[56] Quite frequently, the settling rate and the clarity of supernatant solutions appear to be governed by different parameters.[9,24] Polymers do not replace the metal salt necessary for the charge neutralization,[57] and, therefore, are not effective in removing the fine turbidity of suspended solids. Linke and Booth[3] reported that the fine suspended solids in the supernatant solution carried a disproportionately high dosage of flocculant, and that this resulted in the irreversible stabilization of these particles by protective action.[24]

Since the electrostatic interaction between starch and the mineral surface appears to govern the adsorption of the starch and, hence, the flocculation, the cationic modification of the starch structure is an obvious alternate on highly-negative quartz surfaces(Figure 51). Anionic modification of the starch structure was found to be totally ineffective, or, at best, appreciably less effective for quartz, irrespective of the level of the starch or of the calcium chloride addition (Figures 28 and 29). In addition, the introduction of charged sites in a polymer structure uncoils the chain (intramolecular repulsion) and makes the molecule stretch out, thereby facilitating bridging. The results of the flocculation tests on quartz (Figures 25 and 26) tend to substantiate this interpretation. The maximum settling rates observed on quartz suspensions are appreciably higher than those with corn starch due evidently to the increased adsorption. As a result, the starch levels, where the maximum settling rates are observed, are appreciably higher also.

A closer examination of the settling rate data shows that the cationic starch with higher degree of substitution is less effective as a flocculant. If it is assumed that the two cationic starches have approximately the same molecular weight, too high a degree of substitution with a cationic group may tend to make the adsorbed starch lie down more closely to the negatively charged quartz surface and the conformation of the adsorbed starch would then be less favorable for bridging. The fact that the level of addition of the 0.067 D.S. starch, where the settling rate is maximum, is notably lower than the level of 0.023 D.S. starch supports this interpretation. After a saturation coverage has been reached, the chain interaction between the starch-coated quartz particles might also be hindered due to the electrical repulsion of the cationic groups (intermolecular repulsion). The fact that the maximum settling rate of a goethite suspension when treated with a cationic starch (Figure 27) is somewhat lower than when treated with corn starch (Figure 15) may possibly be accounted for by the unfavorable chain interaction in bridging the particles.

The three limiting cases of the conformation of adsorbed starches thus far discussed may be schematically represented as shown in Figure 53.



coiled (less chance for bridging)

stretched out (ideal for bridging)

stretched out, but too strongly adsorbed (less chance for bridging)

Figure 53. Schematic Representation of the Three Limiting Cases of Conformation of Adsorbed Starch Molecules

In summary, an ideal condition for an efficient flocculation of a quartz suspension entails sufficient adsorption of a starch either through the combined use of such modifying agents as calcium ion, or through a cationic modification of the starch structure, and a stretched-out conformation at the interface for effective bridging. The zeta potential of the suspended matter in the supernatant solution must also be as close to zero as possible in order to effect the clarification of the supernatant solution.

Thus, virtually clear supernatant solutions were obtained when goethite suspensions were treated with an optimum dose of corn starch at near neutral pH (Figures 14 and 15). The supernatant solutions of quartz suspension, however, remained turbid, containing in excess of 500 ppm of solids in suspension irrespective of the pH or the amounts of calcium chloride and corn starch added (Figures 10, 11, 12, and 13). In addition to unfavorable zeta potentials, quartz suspensions aged in an alkaline solution are known to become unusually stable. In fact, they are reported to become non-flocculable with nonionic polyacrylamide.[24] According to Matijevic,[25] colloidal silica may behave as a lyophilic colloid and its destabilization by electrolyte proceeds by a mechanism different from what would be expected for lyophobic colloids. One way to counter the lyophilic nature of the quartz surface may be to change it into a hydrophobic surface with a surfactant. It is well known in ore flotation that a quartz surface can be made hydrophobic with a long-chain alkylammonium salt, thereby rendering the quartz particle floatable upon introduction of air bubbles. At this point the sign of the zeta potential on quartz is reversed.[12,26] These two points, namely, the hydrophobic surface and the reversal of the sign of the zeta potential, become of particular interest in inducing the flocculation condition for quartz suspensions, although it is also known[58] that dodecylammonium ion may interact with a starch molecule to modify its conformation at the quartz surface. The results of a few cursory flocculation tests, presented in Figure 30, showed some promise in clarifying the supernatant solution. Another effective approach in clarifying the supernatant solution of a quartz suspension is through the use of a cationic starch (Figure 26). The role of the cationic starch in reducing the zeta potential of quartz has already been discussed. It is rather puzzling, however, that the cationic polyacrylamide NC 1733 was virtually ineffective in this respect (Figure 31). This may presumably be attributed to a locally excessive concentration of the polymer due to its high adsorbability, particularly on small particles. From a series of tests using a number of cationic polyethyleneimine polymers with different molecular weights, Dixon et al[59] also reached a conclusion that polymers of too high a molecular weight are undesirable.

Physical Factors Affecting Floc Formation

The surface conditions of solids including the adsorbed starch molecules discussed above provide a necessary condition for flocculation; the thermal and mechanical motions of these particles bring them together. The presence of coarse particles in a suspension increases the probability of collision on their descent and also gives weight to each floc for faster settling.[8] The effect of size distribution on flocculation behavior has not been reported in the literature, although occasional mention is made on the flocculation of sized fractions.

The response contours of settling rates for goethite suspensions (Figure 20) and for quartz suspensions (Figure 21) as functions of size moduli and concentrations of solids indicate that, although the settling rates for these two suspensions at given concentrations of solids are seen to increase with increasing size moduli, as anticipated, the settling rates are more strongly dependent on the concentration of solids. No simple relationship may be deduced between the settling rate and the concentration of solids since the settling rate of the goethite suspension decreased monotonically with the concentration of solids whereas that of the quartz suspension increased initially and then decreased. Of course, these observations are at one specific condition only, namely, at pH 9.5 and in the presence of 2 lb of calcium chloride per ton, and the flocculation behavior may change if either the pH or the level of calcium chloride are changed. The difference between the goethite and quartz suspensions appears to lie in their affinity towards a starch flocculant. In a dilute goethite suspension, having high affinity towards starch, only a portion of the suspended particles acquire the flocculant in a relatively high dose, thereby resulting in a high settling rate. The irreversibility of the starch adsorption discussed in connection with the streaming-potential measurements (Figure 39) and the large amount of suspended solids remaining in the supernatant solution appear to support such an interpretation. At higher concentrations of solids the starch may tend to be distributed more evenly and also the mutual interference of the resulting flocs tend to retard the settling rate. The crowding flocs would also have a scouring effect on the suspended matter, particularly when the zeta potential is within that of the critical value.

In the case of quartz the affinity towards starch is not too high, and the distribution of the flocculant throughout a quartz suspension may tend to be more uniform than in a goethite suspension. As a result, the settling rate of a quartz suspension increases with increasing concentration of solids due to increased rate of collision of the particles. Eventually, the mutual interference of the flocs discussed above becomes more significant. It is readily apparent, therefore, that very dilute suspensions of either mineral are very difficult to clarify.

In the coagulation* of mineral suspensions with inorganic electrolytes it is often noted that the clarity of supernatant solutions may be improved with increasing temperature. Increased rate of collision of the particles and increased thermal energy acquired by each particle in surmounting the energy barrier of the interacting double layers[1] might account for this. In the flocculation of quartz and goethite suspensions, however, the settling rate corrected for the viscosity did not increase with the temperature (Figures 22 and 23). The size and the physical properties of flocs must have been affected in a complex manner with the temperature. With an increase in temperature, it is expected that the adsorption, being exothermic, will be adversely affected, and that the conformation of the starch would also be altered due to the thermal motion of the water molecules.

Flocculation Behavior of a Mixture of Minerals

The addition of corn starch to suspensions of certain iron ores resulted in two relatively distinct layers of sediments when the suspensions were permitted to stand. Presumably, the layers were due to the preferential adsorption of the starch on the iron oxide minerals causing them to flocculate and settle more rapidly than the siliceous gangue. In fact, it has been reported in the literature that most starches flocculate aqueous suspensions of hematite, but do not flocculate similar suspensions of quartz.[60] This selective flocculation has been applied in practice to the differential desliming of pulps during the anionic silica flotation of iron ores, resulting in superior metallurgy and lower reagent cost.[61] Recent attempts to extend selective flocculation to other systems, involving such minerals as quartz, calcite, galena, pyrite,and sphalerite, have also been reported.[62,63] This process is considered to be one of the new and most promising approaches to the treatment of minerals that are so finely divided that they are usually either discarded or are tolerated in their interference with conventional processes.[63]

For the successful removal of unwanted siliceous slimes from an oxidized iron ore by selective flocculation, the optimum conditions are extremely sensitive to the mineralogical characteristics of the ore and the mesh-of-grind. It has also been noted that tapioca flour gave better results than corn starch.[9,61] To apply this technique to a variety of refractory iron ores or to cope with the fluctuations in the ore being fed to a plant, the factors governing the selective flocculation must be formulated. The flocculation behaviors of the minerals in the ore, such as are described in the present report, provide the basic information as to the type and the amount of the flocculant, the pH, and the possible effect of impurities either accidentally present or intentionally added. For example, polymers with too high a molecular weight are inherently unsuitable for selective flocculation, and the presence of calcium ions released by the ore may activiate quartz for flocculation with starch. (Although in the Bureau of Mines process calcium chloride is intentionally added.[61]) Cationic starches and polyelectrolytes would be totally ineffective for selective flocculation.

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* In accordance with LaMer's usage, the term "coagulation" is used here for destabilization due to increased ionic strength or to decreased surface potential of particles with inorganic electrolytes, and "flocculation" for a case in which a bridging agent is involved.

The cursory test results on an artificial mixture of goethite and quartz presented in Figure 37 identify a few important parameters, such as the pH and the level of the starch addition, which may be directly correlated with the individual flocculation behaviors and the surface properties given in this report. In a similar manner the most desirable type and molecular weight of the polymer to be used, the effect of the presence of calcium and magnesium ions released by the ore, and the mesh-of-grind may be formulated. Such a process, however, will certainly result in a well-dispersed siliceous slime which must be disposed as tailing and the clarified water returned to the circuit for reuse.[64]

SECTION VIII

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SECTION IX

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